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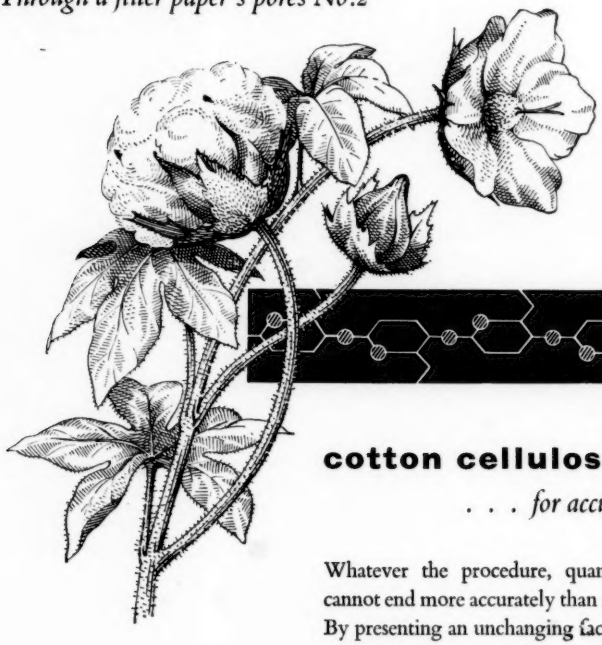

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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

2862. **Determination of masses of materials for micro-analysis below 10^{-6} g by means of electrostatic charging.** H. Straubel. *Z. Electrochem.*, 1956, **60** (9–10), 1033–1036.—A new method of weighing very small samples is described in an apparatus resembling that of the Millikan oil-drop experiment. C. A. FINCH

2863. **Removal of water from organic solvents.** G. Wohlleben (Firma M. Woelm, Eschwege, Germany). *Angew. Chem.*, 1955, **67**, 741–743.—Filtration through an alumina column will produce water-free solvent much more rapidly than by normal techniques. In general, a basic alumina is used, but for acetone and ethyl acetate a neutral alumina must be employed. The method is unsuitable for alcohols. J. H. WATON

2864. **Stability of sodium tetraphenylboron solutions.** S. S. Cooper (The Univ., St. Louis, Mo., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 446–448.—Aq. soln. of 10^{-2} to 10^{-3} *M* $Na(C_6H_5)_4B$ adjusted to a pH of 8 to 9 with NaOH are stable for several weeks even when stored in colourless containers at 26° in diffused light. Soln. between 4×10^{-5} and 4×10^{-4} *M* at pH 10·5 are stable for at least seven days, and obey Beer's law strictly at 240, 250, 262·5 and 272 mμ. The stability of this reagent can be checked from the observed u.v. absorption spectra between 220 and 300 mμ. W. J. BAKER

2865. ***o*-Dithiols in analysis. III. Reactions of toluene-3:4-dithiol in acetate buffer and alkaline solutions: toluene-3:4-dithiol as a reagent for copper, cobalt, iron, antimony and thallium.** R. E. D. Clark (Cambridgeshire Tech. Coll. and School of Art, Cambridge, England). *Analyst*, 1957, **82**, 177–182.—Toluene-3:4-dithiol, hitherto used as a reagent in strongly acid soln., does not form complexes with many metals in NaOH, aq. pyridine or acetate buffer soln., but brilliant colours are formed with Cu, Co, Fe^{2+}, Th, Ni and Mn, and also in the presence of pyridine with V^{4+}, V^{5+}, Ru^{3+} and Sb^{5+}, the last under special conditions. The first seven elements are in order of ease of formation of the complex. The procedure for applying the test to each metal is described. Under the stipulated conditions few other cations interfere, and several of the reactions appear to be specific or can be rendered so in suitable conditions. Any of the elements Cu, Co, Fe^{2+}, Th and Sb^{5+} can be detected in the presence of the others and of all the more common metal cations.

IV. Diacetyltoluene-3:4-dithiol, dibenzoyltoluene-3:4-dithiol and the zinc complex of toluene-3:4-dithiol. R. E. D. Clark. *Ibid.*, 1957, **82**, 182–185.—The keeping qualities of pure toluene-3:4-dithiol are poor and therefore it appeared advantageous to generate it as required from the derivatives now described. The preparation of diacetyltoluene-3:4-dithiol (**I**), dibenzoyltoluene-3:4-dithiol (**II**) and the zinc complex of toluene-3:4-dithiol (**III**) are described. **I** and **II** are hydrolysed by alkali to yield toluene-3:4-dithiol, but are stable in acid, and **I** is hydrolysed slowly by warm aq. pyridine and rapidly by ethanolic K ethoxide. **I** gives colour reactions with Pd^{2+}, Re^{7+}, Te^{4+}, Se^{4+} and Ir^{4+} in conc. HCl. **II** reacts with Pd^{2+} and Se^{4+}. A soln. of toluene-3:4-dithiol suitable for analysis may be prepared from **III** by dissolving it either in ethanol containing a little dil. HCl or in aq. NaOH soln. A. O. JONES

2866. **Metal precipitation with mono- and diphenylarsinic [phenylarsonic and diphenylarsinic] acids.** R. Pietsch (Univ. Graz, Austria). *Mikrochim. Acta*, 1957 (2), 161–166.—The qualitative behaviour of a large number of metal ions with these acids is reported. The pH values at the beginning of pptn. are tabulated. D. F. PHILLIPS

2867. **Use of organic sulphur derivatives in volumetric analysis. IV. Titrations with potassium mercaptophenylthiothiadiazolone [bismuthon].** J. Čihalík and J. Voráček (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 278–282.—A direct polarographic determination of Cu and Cd with bismuthon (**I**) and an indirect potentiometric titration of Bi are described. *Procedure for Bi*—To 0·35 to 3·5 mg of Bi add 1 to 2 ml of 0·05 *M* **I**, adjust the pH to between 2 and 6, add 3 ml of *M* KNO_3, dilute to between 15 and 20 ml and filter off the ppt. Titrate an aliquot of the filtrate with 0·05 *M* $Hg(NO_3)_2$ with potentiometric or polarographic indication. The error is within ±0·44%. *Procedure for Cu*—Copper (0·15 to 3·5 mg) can be titrated polarographically in a vol. of 20 ml, at a pH of 5·5 to 7, in KNO_3 electrolyte, with 0·025 *M* $Hg(NO_3)_2$ (e.m.f. −0·62 V). The error is within ±0·30%. Cadmium can be titrated by the same method. The error is within ±0·34%. For polarographic titrations the system dropping-mercury electrode - satd. mercurous sulphate electrode was used. J. ZÝKA

2868. **Use of the ionisation produced by α-rays for gas micro-analysis.** M. Lefort. *J. Phys. Radium*, 1956, **17**, 164–165.—The dependence on gas composition of the sensitivity of an alphatron-type vacuum gauge is used for the analysis of the two-component mixtures, H - N or O; H - CO_2; N - N_2O or H - ethane. The source is 0·6 mC of $RaCl_2$ on a nickel support. A thin mica film prevents the escape of Rn. As little as 1 cu. mm (s.t.p.) of gas can be analysed with a precision of 10%, improving to 1% with 20 cu. mm. Nitrogen and oxygen cannot be distinguished with this device. CHEM. ABSTR.

2869. **Theory of paper chromatography of inorganic compounds. III. Quantitative treatment of frontal and elution chromatography.** J. Bouzková,

M. Hejtmánek and I. Vavruch (Inst. Phys. Chem., High School of Chem. Technol., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (1), 36–46.—A fundamental and comprehensive theoretical study of a proposed new method for the calculation of the position and distribution of the compound by quant. chromatography on paper strips is presented. For the confirmation of calculated values, the data obtained experimentally for two chlorides of alkali metals were used. J. ZÝKA

2870. **Use of radioactive isotopes in the paper chromatography of inorganic compounds.** E. S. Burkser and G. D. Eliseeva. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 84–88; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1193.—Study is made of the chromatographic separation of the ions Ca^{2+}, Sr^{2+}, Co^{2+} and Fe^{3+}, labelled with the radioactive isotopes ^{45}Ca, ^{89}Sr, ^{60}Co and ^{59}Fe, respectively, with mobile solvents composed of pyridine - H_2O - KSCN (79:20:1) for Ca and Sr, and acetone - H_2O - conc. HCl (87:5:8) for Co and Fe. It is confirmed that the chemical behaviour of the radioactive isotopes is in no way different from that of the stable isotopes. It is shown that the radioactive indicator method may be used for the direct detection of the positions of the zones on the paper chromatograms. By using a preparation of ^{89}Sr contaminated with other radioactive isotopes, it is shown that paper chromatography is a very sensitive method for the evaluation of the degree of radiochemical purity of radioactive preparations. C. D. KOPKIN

2871. **Ion exchange in analytical chemistry. Developments in recent years.** U. Schindewolf (M.I.T., Lab. Nucl. Sci., Cambridge, Mass., U.S.A.). *Angew. Chem.*, 1957, **69** (7), 226–235.—The efficiency of an ion-exchange procedure is determined by the equilibrium constants of the ions which are influenced by different factors such as the eluent and complex formation. Some special applications of ion exchange are described; extensive tables of separation procedures for inorganic ions, with references to the literature, are included. N. E.

2872. **A contribution to the method of flame-photometric analysis.** Gh. Pavloschii and E. Gruia. *Rev. Chim., Bucharest*, 1956, **7** (11), 657–658.—The effect of the presence of different salts in a soln. to be analysed for Na, K or Ca on the conditions of excitation and emission are discussed and a theoretical interpretation of the results is given. Experimental justification for the equations evolved is provided. H. SHER

2873. **Tables for calculating flame-photometric series analyses.** W. Bunge and R. Neuber (Anal. Lab., VEB, Electrochem. Kombinat, Bitterfeld). *Chem. Tech., Berlin*, 1956, **8** (12), 733–735.—Descriptions are given of the construction and use of tables which enable the results of flame-photometric series analyses to be rapidly calculated from the galvanometer deflection of the sample solution and the deflections of the two (higher and lower) comparison solutions. These tables are derived from the Schickmann equation (*Silikattech.*, 1951, **2**, 163) and are worked out for each set of comparison solutions and type of sample solution; for simplicity a standard sample wt. is used. H. L. WHITEHEAD

2874. **Notes on the literature of spectral analysis. II. The wavelength of the potassium lines in Harrison's tables.** J. Knop (Chem. Inst., Agronom. Faculty, Brno, Czechoslovakia). *Chem. Listy*, 1957, **51** (1), 182–185.—A critical, experimental revision is made and new values are determined. J. ZÝKA

2875. **Correlations in ultra-violet spectrophotometry.** R. A. Friedel (Centr. Exp. Sta., Bruceton, Pa., U.S.A.). *Appl. Spectroscopy*, 1957, **11** (1), 13–24.—Phenylnaphthalene-type spectra in related compounds have been noted and spectra and structures of fluorene derivatives are compared. Graphs of intensity as a function of wavelength are discussed with special reference to the spectral effect of three classes of alicyclic rings on the first band in spectra of polynuclear condensed aromatic compounds. Ring-strain effects due to steric hindrance are considered. E. G. CUMMINS

2876. **Purification of hydrocarbons as solvents for ultra-violet spectroscopy.** G. Hesse and H. Schildknecht (Inst. für Org. Chem., Univ., Erlangen, Germany). *Angew. Chem.*, 1955, **67**, 737–739.—Purification of *cyclo*hexane and *n*-heptane for use in u.v. spectroscopy is achieved by treatment with conc. H_2SO_4, followed by filtration through a basic alumina column. A silica gel column is less efficient, but filtration of the solvent through a column containing a layer of silica gel above one of alumina provides a "dry purification," prior treatment with conc. H_2SO_4 thus being avoided. J. H. WATON

2877. **Purification of solvents for spectroscopic purposes. II.** M. Pestemer (Wissensch. Hauptlab., Farbenfabriken Bayer, Leverkusen a Rh., Germany). *Angew. Chem.*, 1955, **67**, 740–741.—Methods for purifying the following solvents are quoted: *n*-heptane, *iso*pentane, 3-methylpentane, methyl-*cyclo*hexane, ligroin, $CHCl_3$, ethanol, diethyl ether, ethyl acetate, pyridine and aniline. References are given to the use in spectroscopy of saturated aq. salt soln., *e.g.*, $Mg(ClO_4)_2$, for dissolving certain organic compounds. The transmittancy of various solvents in the region 15 to 25 μ is discussed. J. H. WATON

2878. **Infra-red spectroscopy as a quantitative analytical method in general chemicals manufacture.** J. C. Hawkes (Monsanto Chemicals Ltd., Ruabon, Denbighshire). *J. Appl. Chem.*, 1957, **7** (3), 123–130.—Applications of i.r. spectrophotometry to the analysis of crude products formed in the manufacture of organic substances, with special reference to the chlorination of phenol and the production of 2:4-dichlorophenoxyacetic acid, and *p*-phenetidine are described. E. G. CUMMINS

2879. **The technical application of infra-red analytical methods.** K. F. Luft (Office Nat. Étud. et Rech. Aeronaut., Chatillon S/Bagneaux, France. *Dechema-Monogr.*, 1956, **27**, 275–285.—The methods and applications of i.r. spectroscopy are reviewed with special reference to the analysis of gas mixtures. A. R. ROGERS

2880. **Infra-red analysis by the derivative method.** G. L. Collier and F. Singleton (R. Graesser Ltd., Sandycroft, Chester, England). *J. Appl. Chem.*, 1956, **6** (11), 495–510.—Derivative i.r. spectra obtained by means of an analogue computer have been used for qual. and quant. analysis. Examples are given of the determination of *m*- and *o*-cresol in commercial *m*-cresol, and of *m*-cresol, *o*-cresol and

phenol in crude tar phenols without prior fractionation and by a single independent measurement for each component. (See Note, *J. Appl. Chem.*, 1957, **7** (4), 204.) K. A. PROCTOR

2881. **Chemical analysis by diffuse reflection spectrophotometry.** R. G. Giovanelli (National Standards Lab., Chippendale, New South Wales). *Nature*, 1957, **179**, 621–622.—The method is very useful for biological problems and can be most readily applied to the visible part of the spectrum and to some extent to the u.v. It is also possible to undertake spectral reflectance measurements in the i.r. regions. The main limitations to the use of the method for chemical analyses are the need to ensure thorough, or at least reproducible, dispersion and the need to obtain at least one absolute chemical analysis if absolute calibrations are required. K. A. PROCTOR

2882. **An introduction to microwave spectroscopy.** I. G. Morgan. *Hilger J.*, 1957, **3** (3), 38–42.—After a brief survey of theoretical principles, practical details of generators, wavemeters, detectors, cells and waveguides are discussed. K. A. PROCTOR

2883. **Radioactivation analysis.** E. N. Jenkins and A. A. Smales (A.E.R.E., Harwell, England). *Quart. Rev. Chem. Soc., Lond.*, 1956, **10**, 83–107.—A review with 72 references. N. E.

See also Abstract 2967.

2.—INORGANIC ANALYSIS

2884. **Potentiometric determination of metals in the form of sulphides with naturally occurring minerals as indicator electrodes.** V. A. Kremer and E. I. Vaĭl' (Mining Inst., Kharkhov). *Zavod. Lab.*, 1957, **23** (2), 146–150.—The method is based on the fact that certain sulphide minerals, *e.g.*, galena, pyrites and particularly argentite, show stable and rapidly established potentials in soln. containing S^{2-}, the potential depending on the concn. of S^{2-}. To prepare an argentite electrode, the mineral is first heated to 850° in the absence of air, a silver wire is attached and the point of contact and the wire are coated with bakelite varnish. A S.C.E. is used as reference electrode. Two methods of determining Cu and Zn in brass are described. In the titration-curve method the sample (0·4 to 1 g) is dissolved in 10 ml of dil. HNO_3 (1 + 1), oxides of N are boiled off, the soln. is diluted to 100 ml in a calibrated flask, and 10 ml is mixed with 20 to 30 ml of an aq. soln. *M* in NH_3 and NH_4NO_3, then heated to between 70° and 80° and titrated with 0·05 to 0·10 *M* Na_2S, standardised separately against Cu^{2+} and Zn^{2+}. The first step in the curve corresponds to Cu and the second, obtained preferably with a fresh argentite electrode, corresponds to Zn. In the second method, which depends on titration to a definite potential, the sample is dissolved as before but the 10-ml aliquot is mixed with 20 ml of the ammoniacal buffer soln. and 1 ml of dil. hydrazine hydrate soln. (1 + 50) and heated to decolorisation at 70° to 80°. The soln. is then rapidly titrated with the Na_2S soln. to a potential of 250 mV, and then dropwise to 350 mV. The electrode is then changed and the titration is carried out rapidly to 550 mV and then slowly to 590 mV. The electrode can also be used for determining the concn. of a soln. of Na_2S by titration with an ammoniacal soln. of Zn. G. S. SMITH

2885. **Determination of mixtures of light and heavy water by means of a simple infra-red photometer.** A. Berton and M. Ceccaldi. *Chim. Anal.*, 1957, **39** (3), 102–103.—Infra-red radiation of $\simeq 1{\cdot}4\ \mu$, obtained from a tungsten-filament lamp, filtered with manganese silicate glass or vitreous selenium, is strongly absorbed by H_2O but not by D_2O. After passing through a 1-cm cell the radiation falls on a thermopile (50 junctions) and is detected as an e.m.f. of about 2 mV with H_2O or 6 mV with D_2O in the cell. The absorption does not obey Beer's law, but a precision of $\pm$ 1% is attainable. E. J. H. BIRCH

2886. **Analysis of hydrogen peroxide by colorimetry.** P. Blanquet and G. Dalmai (Lab. de Chim. Gén., Sorbonne, Paris). *Bull. Soc. Chim. France*, 1957, (3), 419–422.—The colour produced by H_2O_2 in a soln. of UO_2^{2+} and Na_2CO_3 is measured at 380 or 400 mμ. *Procedure*—The subject soln. (10 ml) is made up to 25 ml with a soln. containing uranyl nitrate (2 g) and Na_2CO_3 (100 g) per litre and the absorption (which is stable for 24 hr. and obeys Beer's law) is measured. It is shown that the complex formed contains 1 mol. of H_2O_2 to each UO_2^{2+} ion. Interference by substances likely to be found in combustion products is confined to formaldehyde, which causes fading, so that a determination in its presence should be made in $<$ 1 hr. Acids (which cause formation of bicarbonate) cause no interference in small quantities. E. J. H. BIRCH

2887. **The determination of lithium, sodium and potassium in mixtures with the "EEL" flame photometer.** W. A. Stuart, M. Simpson and W. N. Hardwick (Chem. Engng Div., A.E.R.E., Harwell, England). *Analyst*, 1957, **82**, 200–203.—A rapid method for the determination of Na^+, K^+ and Li^+ in aq. soln. of the mixed chlorides is described. Since these ions interfere with each other and the amount of each may vary in samples it was not possible to produce standard graphs and a bracketing technique was used. The approx. concn. of each element was first obtained by adjusting the sensitivity control to give full-scale deflection. Dilutions were then made to bring the concn. of each element to below 10 p.p.m. and, after the instrument had been set to give full-scale deflection for 10 p.p.m. of the element to be determined, a scale reading was obtained from the diluted sample. This was repeated for each element. From these data two soln. were made from standards differing by $\simeq$ 0·2 p.p.m. of each constituent and bracketing the diluted sample. The bracketing soln. were then used as standards with the diluted sample interposed, and the composition of the sample was obtained by direct proportion. A. O. JONES

2888. **Use of sodium ferrocyanide for the volumetric determination of potassium.** A. S. Kozlov (M. V. Lomonosov State Univ., Moscow). *Zavod. Lab.*, 1957, **23** (2), 157–159.—The method is based on the pptn. of $5Cd_2Fe(CN)_6.4K_4Fe(CN)_6$. The soln. to be analysed is mixed with 10 ml of 0·1 *M* $Ca(NO_3)_2$ (to act as a coagulant), 20 ml of 0·1 *M* $CdSO_4$ and water to give a vol. of $\simeq$ 200 ml. The soln. is treated during continuous stirring with 20 ml of 0·1 *M* $Na_4Fe(CN)_6$ and diluted to 250 ml. After a coagulation period of 5 to 10 min., the soln. is centrifuged at 800 to 1000 rev. per min., and 200 ml of the clear liquid is mixed with 10 ml of conc. H_2SO_4, 4 g of $(NH_4)_2SO_4$, 2 to 3 drops of 1% $K_3Fe(CN)_6$ soln. and 2 to 3 drops of diphenylamine indicator, and titrated with 0·05 *M* $ZnSO_4$

to a lilac colour. The excess (≮ 1 to 2 ml) of the $ZnSO_4$ soln. is titrated during continuous agitation with 0·033 *M* $K_4Fe(CN)_6$ to a sharp transition from grey to green. G. S. SMITH

2889. **Quantitative determination of potassium, sodium and calcium by means of their nitrite complexes.** H. Zimmer (Schliemann Teer-Chemie K.G., Berlin-Britz). *Z. anal. Chem.*, 1957, **155** (5), 337–340.—The colorimetric determination of K, Na and Ca can be made only by indirect methods, since these metals show no characteristic colour reactions. An examination has been carried out of the conversion into nitrite complexes, since these, by diazotising or coupling with aromatic amines, can yield azo dyestuffs capable of being colorimetrically estimated. Zimmer's method (*cf. Anal. Abstr.*, 1957, **4**, 78) was studied and applied with some modifications. Potassium was separated as $K_2AgCo(NO_2)_6$, Na as $6NaNO_2.9CsNO_2.5Bi(NO_2)_3$, and Ca as $K_2CaNi(NO_2)_6$. Comparison with a colorimetric standard showed that the method could be used with advantage. W. J. WRIGHT

2890. **The flame-photometric determination of caesium in bismuth and bismuth - uranium alloy.** P. C. Wildy [U.K.A.E.A. (Research Group), Woolwich Outstation]. A.E.R.E. Report C/R 2114, 1956, 11 pp.—The sample is dissolved in HNO_3 and after being diluted to standard volume the solution is submitted to flame photometry at 8521 A according to standard procedure. Caesium is determined by comparison with a standard, allowance being made for a blank; calibration graphs are presented. Reproducibility data are given; the coefficient of variation is from 1·5 to 15% over the range of Cs concn. of 5 to 0·2% for 11 determinations at each level of Cs.
D. A. PANTONY

2891. **Decomposition of samples by fusion as applied to the polarographic determination of copper, zinc, lead and cadmium.** A. I. Lyakh, E. V. Lisitsina and Z. N. Shisterova (All-Union Sci. Res. Mining Metall. Inst. of Non-Ferrous Metals). *Zavod. Lab.*, 1957, **23** (1), 20–23.—Samples of ores, etc., are decomposed by a mixture of NH_4Cl and NH_4NO_3 (1:1) in a conical flask on a sand bath at 240° to 250°. Completion of the decomposition, which takes 5 to 7 min., is indicated by cessation of gas liberation from the melt. The cooled melt is dissolved in a suitable solvent for the polarographic determinations. G. S. SMITH

2892. **Use of qualitative reactions for the colorimetric determination of copper and nickel.** M. M. Raĭnes and Yu. A. Larionov. *Trudy Komiss. Anal., Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 295–299; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1215.—The microchemical reaction for the detection of Cu, based on its catalytic action on the oxidation of quinol with H_2O_2 in the presence of pyridine, may be used for the photometric determination of Cu. To 10 ml of a $CuSO_4$ soln., containing 0·2 to 5 mg per litre of Cu, add 1 ml each of a 0·1% soln. of quinol, H_2O_2 and a 5% soln. of pyridine. After 10 min. add 1 ml of 5% acetic acid and immediately measure the extinction with a blue filter. Small quantities of Ni and Fe do not interfere. The optimum value for the pH is 3 to 3·5. To determine Ni, add to 10 ml of the soln. one drop of reagent (prepared by heating to boiling-point a mixture of 3·75 ml of 40% formaldehyde, 3·5 g of hydroxylamine hydrochloride and 3·75 ml of water), and 0·4 to 1·0 ml of *N* NaOH. Measure the extinction without a filter. C. D. KOPKIN

2893. **o-Hydroxyacetophenone oxime as an analytical reagent. II. Gravimetric estimation of copper and nickel and their separation from other metals.** S. N. Poddar (Indian Ass. for the Cultivation of Science, Calcutta). *Z. anal. Chem.*, 1957, **155** (5), 327–334 (in English).—*o*-Hydroxyacetophenone oxime (**I**) remains stable for months at room temp. It is not decomposed by hot water, in which it is slightly sol., so metal ppt. can be readily washed free from entrained reagent. In this respect, **I** has an advantage over salicylaldoxime. The separation of Cu from a mixture with Ni is carried out by pptn. with **I** at pH 2 to 3; Ni is completely pptd. from the filtrate by adjusting the pH to between 5 and 5·5. At controlled pH, Cu can be determined in the presence of Pb, Hg, Cd, As, Co, Mn, Zn, U, Mg and phosphoric acid. If Fe^{III}, Sb, V and Bi are present they can be masked by tartaric acid; Ni can be determined without interference in the presence of Pb, Hg, Zn, Cd, Mn and Mg; Fe^{III} and Bi, if present, are masked by tartaric acid. If Co is present in quantities four times as great as that of Ni, a slightly high value for Ni is obtained.
W. J. WRIGHT

2894. **New gravimetric and volumetric method for determination of silver.** P. Spacu and T. I. Pirtea. *Rev. Chim., Bucharest*, 1956, **7** (8), 481–483.—The procedure is based on the reaction of Ag with sodium nitroprusside (**I**), which gives a cream ppt. of $Ag_2[Fe(CN)_5(NO)]$, unaffected by light, stable, and insoluble, with mol. wt. greater than that of the usual halogen complexes. Pptn. is rapid and complete at room temp., and ppt. can be filtered immediately, and after washing can be dried in a vacuum desiccator or even in an oven at 110°. If modified the method can be used in the presence of Pb and Zn. *Gravimetric method*—To 10 to 30 ml of a neutral or acid soln. of Ag^+ at 50° to 60° add 1 to 2 g of solid NH_4NO_3 followed by approx. 0·1 *N* **I**. A yellow - red colour of the supernatant liquid indicates complete pptn. and excess of **I**. Filter immediately through a sintered glass crucible, washing with NH_4NO_3 soln. (3%), water, ethanol and ether. Dry in a vacuum desiccator and weigh. The determination takes 1 to 1·5 hr. In the presence of Pb or Zn the ppt. is washed 4 to 5 times with aq. NH_4NO_3 soln. (3%) heated to between 50° and 60°. *Volumetric method*—Since addition of **I** soln. to $AgNO_3$ soln. leads to the formation of a colloidal ppt., the determination is carried out by running $AgNO_3$ soln. into a known vol. of **I**. This gives a good end-point with or without eosin as an adsorption indicator. Results are consistently ≃ 0·2% high. H. SHER

2895. **Bismuthiol II as an analytical reagent. VII. Estimation and separation of silver from precious metals.** Anil Kumar Majumdar and Bhu Ratna Singh (Jadavpur Univ., Calcutta, India). *Z. anal. Chem.*, 1957, **155** (3), 166–168 (in English).—A 0·5% aq. soln. of the potassium salt of bismuthiol separates Ag from Os, Ir, Ru and Rh in the pH range 5 to 9 when EDTA (disodium salt) is present to complex the interfering ions. In the presence of $Na_2S_2O_3$, the bismuthiol reagent separates Ag from Os, Ir, Ru, Rh and Au between pH 8 and 9. Silver is separated from Pd in cyanide soln. at pH 6, but the separation from Pt is unsatisfactory.
J. H. WATON

2896. **Polarographic titrations with a rotating platinum electrode. IV. Micro-determination of silver in copper alloys and soldering metals.** I. Bozsai (Central Material-Testing Dept., Iron and Metal Works of Csepel, Budapest). *Magyar Kém. Foly.*, 1956, **62** (11–12), 386–389.—Dissolve the sample in conc. HNO_3 containing a little H_2SO_4. To 20 ml of this soln. (containing not more than 5 mg, and preferably 1 to 2 mg, of Ag) add gum arabic (**I**) soln. (2%) (5 ml) and conc. HNO_3 (5 ml), and dilute to 100 ml with water. (The optimum vol. is 50 to 100 ml.) Add an excess of 0·01 *N* KBr and after 1 to 2 min. back-titrate with 0·01 *N* $AgNO_3$; polarise the rotating platinum electrode to + 0·05 V. The limit of determination is 1 mg of Ag in 50 ml; the accuracy then is within ± 0·5%. Higher concn. of HNO_3 or lower concn. of **I** decrease the accuracy. Even a 1000-fold excess of Cu does not interfere. Metals containing 0·1 to 95% of Ag can be determined. The direct titration of the HNO_3 soln. by means of 0·01 *N* HCl is less satisfactory. A. G. PETO

2897. **The use of inhibitors in analytical chemistry. The assay of traces of silver and mercury by the use of a ceric sulphate - sodium arsenite - sodium iodide system.** T. E. Braun (Inst. Méd.-Pharm., Targu-Mures, Romania). *Mikrochim. Acta*, 1957, (1), 128–130 (in French).—The inhibiting effect of traces of Ag and Hg on the oxidation of KI by $Ce(SO_4)_2$ is used for a sensitive assay procedure. A drop of KI soln. is placed on the base line of a sheet of chromatographic paper, followed by a measured quantity of a soln. containing 0·005 to 0·05 μg of Ag or Hg. The paper is suspended in a soln. comprising cerium soln. [ceric ammonium sulphate (10 g) dissolved in 100 ml of cold H_2SO_4 and filtered] (1 part), arsenite soln. (5 g of As_2O_3 dissolved in 7 ml of 30% Na_2CO_3 soln., diluted to 100 ml with H_2SO_4) (1 part) and *N* H_2SO_4 (2·5 parts) until the solvent front reaches nearly the top of the paper. The paper is dried and examined under u.v. light. The length of the non-fluorescent zone is proportional to the amount of Ag or Hg applied at the origin. P. S. STROSS

2898. **Chromatographic detection of silver, lead and mercury cations.** K. Shalvarev. *Tekhnika (Bulg.)*, 1956, **5** (2), 37–38; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,261.—The chromatography is carried out on a silica-gel column (length 10 cm, internal diam. 4 mm, particle size 0·09 mm). Three drops of a soln. of a mixture of Ag^+, Pb^{2+} and Hg^{2+} (0·01 *N*, pH 1) are passed through the column, followed by three drops of 0·01 *N* KI soln. There is formed a pale-yellow zone of AgI, a yellow zone of PbI_2 and an orange - red zone of HgI_2.
C. D. KOPKIN

2899. **Use of silver permanganate in analysis. VII. Thermal decomposition of silver permanganate.** V. Šatava and J. Körbl (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (1), 27–35.—The decomposition of $AgMnO_4$ at temp. up to 1000° was studied by methods of thermal analysis and electrical conductivity measurements. Explanations of the processes of decomposition and of its oxidative catalytic properties in elementary organic analysis are proposed. J. ZÝKA

2900. **A new rapid precise method for gravimetric determination of beryllium.** T. I. Pirtea. *Rev. Chim., Bucharest*, 1956, **7** (7), 427–429.—The amphoteric character of Be, which forms easily soluble beryllates and salts that readily hydrolyse, hinders the formation of a single stable complex. This difficulty is overcome by combining Be with a suitable complex ion, and then with a second one. This is achieved by treating soln. of Be^{2+} with conc. soln. of ammonium carbonate. The sol. beryllium complex thus formed is treated with a conc. soln. of hexa-amminocobalt chloride, which gives a very insoluble cryst. yellow ppt. of $[(H_2O)_2Be_2(CO_3)_3(OH)_3][Co(NH_3)_6].3H_2O$, which is easily washed and dried in a vacuum desiccator. The method is simple and quick (40 to 50 min.), and can be used in the presence of alkaline metals and Fe. Since the Be content of the ppt. is only 4·1%, accurate determination of small quantities is possible. H. SHER

2901. **Photometric determination of magnesium with Eriochrome black T in zinc and its alloys.** H. Pohl (Bundesanstalt Materialprüfing, Berlin-Dahlem). *Metall*, 1956, **10**, 709–711.—Magnesium contents of 0·002 to 0·2% can be determined by this method. The soln. must be freed from disturbing elements and excess of reagents by treatment with oxine and extraction with $CHCl_3$, after which it is treated with a soln. of Eriochrome black T reagent in a soln. buffered at pH 10·6. A red complex is formed, which is photometrically measured against standards. CHEM. ABSTR.

2902. **Quick, accurate method for magnesia determination.** H. E. Gerhard (Lehigh Portland Cement Co., Coplay, Pa., U.S.A.). *Rock Prod.*, 1957, **60** (2), 117–118, 120.—In the usual quant. analysis of cement or limestone the MgO can be determined in ≃ 20 min. in the filtrate from the oxalate separation of Ca. *Procedure*—To an aliquot (100 or 150 ml) add ammoniacal buffer soln. of pH 10 (15 ml), conc. aq. NH_3 (10 ml) and 3% H_2O_2 (20 ml), stir well and allow the mixture to stand for ≮ 15 min. to remove the excess of oxalate ions. Then add 1% (w/v) ethanolic soln. of Eriochrome black T until the colour is wine red, and titrate with 0·1 *N* EDTA (disodium salt) to a pure-blue or -green end-point. The standard deviation is ± 0·03 (six analyses); the results agree with those of the $Mg_2P_2O_7$ method.
W. J. BAKER

2903. **Determination of oxygen in magnesium metal.** Nakaaki Oda and Shigeji Sawabe (Takaoka Plant, Nippon Soda Co. Ltd., Takaoka, Toyama Prefecture). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1956, **59** (12), 1445–1446.—Magnesium oxide fails to react with a dry alkyl halide. Magnesium metal (5 g) is treated with a mixture of diethyl ether and ethyl bromide (3 + 1, by vol.) in a sealed tube filled with an inert gas, and filtered with a sintered glass filter. The tube is washed with saturated boric acid soln. [to decompose Mg(OH)Br produced from MgC_2H_5Br]. The residue (MgO) is thoroughly washed with water, and then dissolved in HCl and determined by the usual method. The mixed solvent must be dehydrated by distillation with metallic Mg. The recovery of MgO is > 95% and the overall deviation is < 7% for < 0·1% of O.
K. SAITO

2904. **Amperometric determination of calcium in limestone by the use of an indicator.** Yu. I. Usatenko and M. A. Vitkina. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 155–161; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1219.—In the determination of Ca amperometrically, Cu^{2+} are used as indicator. Moisten the sample (0·05 to

0·06 g) of limestone and dissolve in a small quantity of HCl. Add 10 ml of 0·1 *M* NH_4Cl soln., dilute to 20 ml and boil to remove CO_2. To the cooled soln. add an equal vol. of ethanol, 0·2 to 0·3 ml of $FeCl_3$ soln. (0·1 *M*, slightly acid with HCl), neutralise to methyl red with 50% aq. NH_3 and add one or two drops in excess. Insert a rotating platinum electrode and a mercury iodide half-cell having a low positive potential, joined to the titration vessel by an agar bridge. Stir and add 0·01 *M* $CuCl_2$ soln. dropwise till the galvanometer needle is on the scale, then titrate slowly with 0·1 *M* ammonium oxalate soln. Trace the portion of the curve near the end-point in intervals of 0·01 ml. A blank is carried out in the same way on the indicator; elements usually found in limestones do not interfere.

C. D. KOPKIN

2905. **Rapid method for the determination of calcium in the presence of magnesium.** G. B. Pasovskaya. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 272–275; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1218.—To determine Ca in the presence of Mg, add to the soln. in a conductimetric titration apparatus 1 ml of a satd. alcoholic soln. of magneson II and 0·5 ml of aq. NH_3 (1:2), dilute to 20 ml and titrate with *N* K oxalate soln. which has been standardised against $CaCl_2$ soln. With a Mg to Ca ratio of 7:1, the addition of standard $CaCl_2$ soln. is recommended, with dilution to give a $CaCl_2$ concn. of 0·01 to 0·02 *N*. The max. error is ≯ 0·97%. The determination takes 20 min. The presence of K and Na does not cause interference.

C. D. KOPKIN

2906. **Emission-spectrographic method for the determination of strontium in silicate materials.** K. K. Turekian, P. W. Gast and J. L. Kulp (Lamont Geol. Observatory, Columbia Univ., Palisades, N.Y., U.S.A.). *Spectrochim. Acta*, 1957, **9** (1), 40–46.—In order to diminish the effects of a varying matrix, samples are mixed in an equal ratio by weight with $CaCO_3$, purified by an ion-exchange technique. Roughly 5-mg samples are arced to completion at 16·5 amp. (anode excitation), in deep electrodes which prevent spattering and allow CO_2 and adsorbed water to escape during the first few seconds of arcing. Working curves are derived from the intensity ratios Sr 4607 A:Ca 4579 A for a series of standards. The coefficient of variation is of the order of ± 7 to ± 12%; comparison analyses with the stable isotope dilution method indicate a fair degree of accuracy.

K. A. PROCTOR

2907. **Determination of strontium by X-ray fluorescence spectrometry.** C. A. Lucchesi (Shell Development Co., Houston, Texas, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 370–373.—By using the North American Philips X-ray fluorescence spectrometer attachment Type 52157A in conjunction with the basic X-ray diffraction source unit, Sr in a 100-mg sample of impure anhydrite was determined in 30 min. with a standard deviation of 0·005% of Sr over the concentration range 0·005 to 0·4%. Yttrium is used as an internal standard to facilitate correction for matrix absorption. Calcium does not interfere. Calibration data are tabulated and sample-preparation technique is discussed.

E. G. CUMMINS

2908. **Flame-photometric determination of small traces of barium in material containing barium sulphate.** E. Pungor and E. É. Zapp (Eötvös Univ., Budapest, Hungary). *Mikrochim. Acta*, 1957, (2), 150–158.—A new procedure for decomposing $BaSO_4$ is described. Decomposition is accomplished with the aid of fluorosilicic acid generated *in situ* with the sample from SiO_2 and HF. The resulting H_2SO_4 is reduced with HI. When disintegration of $BaSO_4$ is complete, the Ba is converted into $BaCO_3$ in the presence of oxalic acid. *Procedure*—Weigh a sample containing 10 to 20 mg of $BaSO_4$ into a platinum crucible. Add SiO_2 (50 mg) which has been purified several times by heating with HCl, HI (70%) (3 ml), HF (40%) (3 ml) and oxalic acid (0·5 g). Evaporate to dryness on a water bath and add HI (3 ml) and HF (2 × 3 ml). Re-evaporate to dryness and heat at 200° to 300° on a sand bath for 30 min. and then dissolve the contents of the crucible in HCl (20%), with heating. The barium content of the resulting soln. is determined by flame photometry, with a Beckman flame photometer, at 870 mμ. A linear calibration graph is obtained provided that the photometer is operated without an extraction duct. The most favourable concn. range of Ba lies between 10^{-4} and 10^{-2} mole per litre. As traces of H_3PO_4 cause suppression of the Ba emission in the flame, it is recommended that HI free from H_3PO_4 be used. An addition of a soln. containing 2×10^{-2} mole of Al per litre is made to both sample and standard soln. in order to even out effects on Ba emission caused by variable contents of Al present in the samples. On the mean of duplicate determinations the range of single results does not in general exceed ± 3% of the content of Ba (13 samples). The mean error of a single result is 2·1%, and the error of the mean of duplicates is 0·43%. The method has been employed on about 400 samples of silicate rock containing barium sulphate.

D. F. PHILLIPS

2909. **Quantitative determination of zinc using tetramethyldiaminodiphenylantipyrinylcarbinol.** Z. A. Abramova and V. P. Zhivopistsev. *Uch. Zap. Molotovsk. Univ.*, 1955, **9** (4), 167–169; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,269.—In the presence of SCN^-, tetramethyldiaminodiphenylantipyrinylcarbinol (**I**) forms with Zn a slightly sol. complex. The high sensitivity of the reaction (limit of detection 2 to 3 μg of Zn per ml) is explained by the sharp colour change in the process of complex formation. The composition of the ppt., $(C_{28}H_{31}N_4O)_2[Zn(SCN)_4]$, is const. The acidity of the Zn^{2+} soln. must be 0·5 to 1·5 *N* in HCl or H_2SO_4. In the presence of Fe^{III} some of the NH_4SCN soln. is added first, followed by a few drops of 10 to 15% ascorbic acid soln. to discharge the colour; then the remainder of the NH_4SCN is added. The ppt. is filtered off, and washed with 0·5 *N* HCl containing 1% NH_4SCN and 0·1% of **I**, then with 0·1 *N* HCl containing 0·5% NH_4SCN and 0·1% of **I**. The ppt. is dried at 105° to 110°. The conversion factor for Zn is 0·0556. No interference is caused by Mn, Cr, Ni, Mg, alkaline earths or alkali metals.

C. D. KOPKIN

2910. **Spectrochemical determination of cadmium and lead in zinc concentrates and agglomerates.** I. Perman and E. Nauta. *Rep. J. Stefan Inst., Ljubljana*, 1956, **3**, 195–201 (in English).—Cadmium and lead have been determined in zinc sulphide ore concentrates and agglomerates within concn. ranges of 0·001 to 1%, by using as excitation sources the d.c. arc of 8 amp. between carbon electrodes and the total combustion method. Excitation conditions are discussed. The line pairs Cd 3261 - Zn 3282 and Pb 2833 - Bi 3067 were used. A

change in composition within the usual limits does not affect the intensity ratio. An accuracy within about ± 7% has been attained. O. M. WHITTON

2911. **Volumetric determination of mercury using tetramethyldiaminodiphenylantipyrinylcarbinol.** V. P. Zhivopistsev. *Uch. Zap. Molotovsk. Univ.*, 1955, **9** (4), 163–166; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,270.—Tetramethyldiaminodiphenylantipyrinylcarbinol (**I**) reacts in acid medium with HgI_4^{2-} to form a slightly sol. complex; excess of **I** forms a red colour. Add to the acidified soln. of Hg about 1 g of KI, then HCl to 0·7 to 1·5 *N* and 2 to 3 ml of benzene (to collect the ppt. formed on the surface). Titrate with a 0·01 *N* soln. of **I** in *N* HCl till the aq. phase turns red. No interference is caused by Mn, Zn, Al, Fe^{II}, Mg, alkaline-earth or alkali metals. Ferric iron is reduced with 10% ascorbic acid soln.; 1 to 2% of Cu does not interfere. The relative error is 3 to 4%. C. D. KOPKIN

2912. **Use of alumina columns in the determination of mercury as dithizonate.** M. D. J. Isaacs, P. Morries and R. E. Stuckey (British Drug Houses Ltd., Graham Street, London). *Analyst*, 1957, **82**, 203–206.—After destruction of organic matter and preliminary extractions, the acidity of an aliquot of the extract is adjusted to 1 to 2 *N* with H_2SO_4 and the soln. is extracted with a chloroform soln. of dithizone in the presence of hydroxylamine hydrochloride. The dark-green extract is applied to the top of an alumina column surmounted by a short column of anhyd. Na_2SO_4. Extraction of the sample soln. is continued with chloroform until the extract is colourless, the extracts being added to the column. Elution of the column is continued with chloroform. Below the brown band of excess of dithizone a rapidly descending orange band of mercury dithizonate appears, and as this approaches the base of the column the eluate is collected separately until it emerges colourless. The vol. is adjusted and the extinction is measured at 490 mμ and referred to a calibration graph. Interference by Cu is minimised and Zn does not interfere although it appears as a red band at the top of the column. Recovery of Hg in the presence of Cu ranged from 90 to 105%. The keto - enol tautomerism of mercury dithizonate is discussed.
A. O. JONES

2913. **Chemical analysis by the use of catalysed or induced reactions. X. Determination of mercury by the use of a photochemically induced reaction with oxalate in the presence of manganese.** Shukichi Sakuraba (Faculty of Engng, Shizuoka Univ., Oiwake, Hamamatsu). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (10), 1528–1532.—A mixture of oxalate (**I**), Mn^{2+} and Hg^{2+} yields a ppt. of HgCl in a weakly acid soln. under u.v. light. The rate of pptn. increases with increasing temp., time of illumination and the concn. of the precipitant. It is likely that the Mn oxalate complex, which induces the reduction of Hg^{2+} with **I** (*Anal. Abstr.*, 1956, **3**, 2664), is formed as an intermediate product. Sodium oxalate (0·1 *M*, 15 ml) is mixed thoroughly with 10% KCl soln. (1 ml) and adjusted to pH 3·2 with *N* H_2SO_4 or HCl. To this soln. are added $MnSO_4$ (0·015 *M*, 7 ml) and the sample soln. (< 0·1 g of $HgCl_2$ per 20 ml). The product is exposed to sunlight or a mercury lamp for ≃ 80 min. The pptd. HgCl is filtered off, washed with water and dried at 110°. Dissolved O in the soln. acts as an inhibitor for the catalytic action; the time of illumination can be markedly reduced when the O is previously removed. Heavy metals such as Au, Pt or Pd are also reduced under the given conditions. K. SAITO

2914. **Determination of organic compounds of metals by the extraction method. X. Extraction and photometric determination of mercury and palladium with phenazone and potassium iodide.** Emiko Sudo (Inst. for Iron, Steel and Other Metals, Tohoku Univ., Katabira-cho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (10), 1446–1449.—The iodomercury complex is insol. in $CHCl_3$; it is extracted, however, by $CHCl_3$ from an acid soln. (0·1 to 1·3 *N* HCl, 0·4 to 1·5 *N* HNO_3 or 0·4 to 1·3 *N* H_2SO_4) in the presence of phenazone (**I**). The sample is mixed with 2 *N* HCl (5 ml), 5% **I** soln. (2 ml) and 10% KI (1 ml) and immediately extracted with $CHCl_3$ (5 ml). The extinction at 330 mμ is proportional to the concn. of Hg for concn. < 80 μg per 5 ml. The presence of Cu, Al, As, Bi, Sb, Fe and Pd vitiates the estimation. Palladium can also be extracted under similar conditions and determined photometrically at 340 mμ. The working curve is linear for concn. of < 20 μg of Pd in 5 ml of $CHCl_3$.

XI. Extraction and photometric determination of a small amount of iron in aluminium, magnesium, zinc and lead metals. Emiko Sudo. *Ibid.*, 1956, **77** (10), 1449–1451.—The photometric determination of Fe with KSCN and **I** (*cf. Anal. Abstr.*, 1955, **2**, 2098) was applied. Metallic Al or Mg (0·5 to 2 g) containing 0·0002 to 0·2% of Fe is dissolved in 6 *N* HCl (20 to 40 ml) and made up to 50 to 500 ml according to the content of Fe. A 5 to 10-ml portion (< 10 μg of Fe) is treated with 20% KSCN (3 ml) and 5% **I** soln. (3 ml), diluted to ≃ 20 ml, and extracted with ethyl acetate (5 ml); the extinction is measured at 470 mμ. Zinc containing > 0·02% of Fe is analysed similarly; when the content of Fe is < 0·02%, the sample (≃ 10 g) is dissolved in dil. aqua regia (HNO_3:HCl:H_2O = 1:3:9) (≃ 150 ml) and treated with aq. NH_3 soln. The ppt. is dissolved in 6 *N* HCl (10 ml), diluted to between 100 and 250 ml and a 5 to 10-ml portion is treated with KSCN and **I** and the extinction measured as before. Lead (0·5 g) containing > 0·005% of Fe is dissolved in dil. HNO_3 (1 + 4) (10 ml), diluted, and similarly treated. When the content of Fe is < 0·005%, Pb is pptd. as sulphate and the filtrate is treated as above. The presence of Cu and Bi (in concn. greater than that of Fe) vitiates the estimation.

XII. Extraction and photometric determination of molybdenum with sodium diethyldithiocarbamate. Emiko Sudo. *Ibid.*, 1956, **77** (10), 1451–1453.—The yellow ppt. of Mo diethyldithiocarbamate is soluble in $CHCl_3$, and the extinction at 340 and 250 mμ is proportional to the concn. of Mo for < 50 and < 5 μg per ml, respectively. The sample soln. from which Mo is extracted must be 0·3 to 2·5 *N* acid with HCl. This method is applicable to a quick (< 30 min.) determination of Mo in iron; most Fe is removed as $Fe(OH)_3$ and the small amount of remaining Fe is masked with tartrate. *Procedure*—Dissolve the sample (2 g) in HCl soln. of Na_2HPO_4 (60 g of $Na_2HPO_4.12H_2O$ in 1 litre of 8 *N* HCl) (30 ml), treat with H_2O_2, neutralise with NaOH until the ppt. of phosphate appears, make acid with a few drops of HCl, treat with 6 *N* NaOH (≃ 25 ml) and make up to 250 ml. Make a 10-ml portion of the supernatant liquid acid (*N* in HCl), mix with 0·1% aq. Na diethyldithiocarbamate soln. (2 ml) and extract with $CHCl_3$ (5 ml). K. SAITO

2915. **The colorimetric micro-determination of boron.** M. Basset and G. Martin (Lab. Chim. Agric. Biol., 292 rue St. Martin, Paris). *Bull. Soc. Chim. Biol.*, 1957, **39** (2–3), 337–341.—The method, valid up to 4 μg of B, depends on the colour reaction with Chromotrope 2B (**I**) in sulphuric and acetic acids (*cf.* Martin, *Anal. Abstr.*, 1954, **1**, 2634). Vegetable tissues are ashed with MgO at 600° to 700°, in a quartz dish (not platinum, which gives a colour with **I**), soil extracts are evaporated with MgO then ashed, and fruit juices are absorbed on ashless filter-paper that has been impregnated with MgO, then dried and ashed. (A filter-paper blank must then be examined, as some papers contain traces of B.) Water should be distilled from quartz or stainless steel (not Pyrex glass), and boron-free glassware employed. The ashed residue is dissolved in a soln. of hydroxylamine hydrochloride (150 ml, 6%), hydrazine hydrate (2 ml, 99%) and glacial acetic acid (to make 1 litre), at such a rate that the soln. contains $\geqslant$ 2 μg of B per ml. This soln. (2 ml) is treated with 2 ml of a soln. of **I** (0·05%) in a mixture of equal vol. of conc. H_2SO_4 and glacial acetic acid, followed by 7 ml of a mixture of equal vol. of glacial acetic acid and acetic anhydride. After 45 min. the extinction is read in a 1-cm cell in filtered light (590 to 630 mμ), and the reading referred to a calibration curve.

R. E. Essery

2916. **Ultra-violet absorptiometric determination of boron in aqueous medium using chromotropic acid.** D. F. Kuemmel and M. G. Mellon (Purdue Univ., Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 378–382.—From 0·005 to 0·12 mg of B, equiv. to 0·1 to 2·4 p.p.m. in 50 ml of soln., can be determined rapidly from the observed decrease in extinction between 355 and 380 mμ caused by the addition of H_3BO_3 to a dil. soln. (pH $\simeq$ 7) of chromotropic acid. *Procedure*—Adjust the aq. soln. of the sample to a pH between 4·5 and 6·5 so that the final vol. is $\geqslant$ 15 ml. Add 25 ml of 0·00028 *M* aq. disodium chromotropate plus 10 ml of 2 *M* aq. sodium acetate, dilute to 50 ml and mix. Avoiding exposure to strong light, place this soln. in the reference cell and the blank (reagent plus buffer) in the sample cell of a Cary recording spectrophotometer (1-cm quartz cells, slit width $\geqslant$ 0·25 mm). Balance the instrument at 400 mμ and then scan down scale to 350 mμ. Calculate the concn. of B by referring the extinction of the differential peak at 361·5 mμ (max. change) to a calibration curve for soln. containing $\geqslant$ 0·12 mg of B per 50 ml. The accuracy is satisfactory.

W. J. Baker

2917. **Tests for aluminium and hydroxytriphenylmethane dyes.** F. Feigl and D. Goldstein (Min. Agric., Rio de Janeiro, Brazil). *Anal. Chem.*, 1957, **29** (3), 456–458.—In basic soln. Al^{3+} react with hydroxytriphenylmethane dyes to give coloured chelate compounds having considerable resistance to HCl and H_2SO_4. With Chrome-fast pure blue B as the reagent as little as 0·1 μg of Al can be detected, and the colour reaction can be employed for specific detection of alumina and also for traces of Al in water and silicates. Hydroxytriphenylmethane dyes can be detected by their reaction with Al^{3+}, the limits of detection being from 0·1 to 5 μg.

G. P. Cook

2918. **Critical examination of the determination of hydrogen in aluminium and aluminium alloys by the method of solution in bromine - carbon disulphide.** W. Mannchen and W. Fischer (Bergakademie, Freiberg/Sa., Germany). *Metall*, 1956, **10** (5–6), 191–195.—The method of Chrétien *et al.* (*AlumArch.*, 1939, 23) has been critically examined. The method depends on dissolution of the sample, comprising fine turnings of aluminium or aluminium alloy, in CS_2 - Br. Hydrogen present in the metal is converted into HBr. This, protected by a slow stream of N, is led into dil. $AgNO_3$ soln. The weight of AgBr obtained is then calculated back to vol. of H. After describing their own apparatus and modifications made to the original method, the authors describe reproducibility tests, results of which, for a single determination, are in accordance with those of the original authors. However, investigations on the relationship between AgBr recovered and weight of sample taken show that the curve consists of two portions: a steeply sloping exponential portion for sample weights up to about 2·5 g, and a linear portion for sample weights from about 2·5 to 4 g. The original authors had carried out their measurements in the flat linear region of the curve. An explanation offered is based on the assumption that a hydrolysis reaction takes place between Al_2Br_6 initially formed and traces of moisture present in the apparatus. Experiments were carried out to ascertain whether the method is specific for H or whether there might be an effect due to varying phosphorus contents of the sample. The latter possibility was to some extent confirmed. It is considered that the method in its present form is not valid and no means can be suggested for eliminating the difficulties.

D. F. Phillips

2919. **Indirect colorimetric determination of indium.** Tôru Nozaki (Fac. of Engng, Ehime Univ., Niihama, Ehime Prefecture). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1751–1752.—Indium is pptd. as $[Co(NH_3)_6]InCl_6$ from 2·4*N* HCl. in the presence of twice its equiv. of $Co(NH_3)_6Cl_3$. The ppt. is dissolved in a small amount of water, the Co is pptd. with Na_2S, and is determined colorimetrically with nitroso-R salt by the same procedure as for Tl (*Anal. Abstr.*, 1956, **3**, 2993).

K. Saito

2920. **Gravimetric determination of cerium and thorium in minerals.** S. Lupan. *Rev. Chim., Bucharest*, 1956, **7** (11), 661–665.—In the analysis of monazite and other minerals, Ce and Th may be separated from other elements by removing Si with H_2SO_4 and HF and heating the residue for several hours with conc. HCl and KI to bring the Ce and Th into soln. These elements may be pptd. quant. together by oxalic acid at pH $\simeq$ 1 in the absence of HCl; Ce must be converted into the tervalent form by treatment with H_2O_2. The minimum amount of both elements that can be determined gravimetrically is 0·5 mg in a vol. of 20 to 30 ml after standing overnight. Phosphate may be removed by double pptn. in conc. oxalic acid soln. adjusted to pH 1. Calcium is pptd. as oxalate under these conditions and must be removed by igniting the ppt. and pptg. the Ce and Th as hydroxides. Small amounts of Fe_2O_3 and Al_2O_3 have little influence on amounts of Ce and Th $>$ 10 mg, but for smaller amounts the oxalates must be pptd. with Ca oxalate and subsequently separated. Separation of Th from Ce is effected by pptn. of the Th as iodate; when $<$ 20 mg is present, re-pptn. as oxalate in the presence of HCl is necessary. Losses of Th vary from 10% on 10 mg to 2% on 100 mg.

H. Sher

2921. **Separation and determination of radiocerium by liquid - liquid extraction.** G. W. Smith and F. L. Moore (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 448–451.—Trace or macro amounts of Ce in fission products can be separated from contaminants (Eu, Ru, Zr, Pa, Pu, Np and others) by procedures based on the extraction of Ce^{4+} into 0·05 *M* 2-thenoyltrifluoroacetone - xylene from *M* H_2SO_4 soln. containing 0·1 *M* $K_2Cr_2O_7$ and 0·2 *M* $NaBrO_3$, whereby a stable cerium chelate, sol. in xylene, is formed. In the tracer method the org. phase after extraction is stripped with an equal vol. of 10 *N* HNO_3, and ^{144}Ce is counted directly in an aliquot of the aq. strip. In the macro method, Ce oxalate (0·8 mg per ml) is used as carrier, and the Ce in the aq. strip can either be determined directly by counting (in an aliquot) or gravimetrically as $Ce_2(C_2O_4)_3 \cdot 10H_2O$, followed by counting $\simeq$ 3 hr. after the final pptn. The carrier method takes $\simeq$ 1 hr. and yields of ^{140}Ce or ^{144}Ce are $\simeq$ 80%; the accuracy is within $\simeq \pm$ 2%. The sample soln. should be free from Cl^-, F^- and PO_4^{3-}. Variables and specific applications of the methods in fission-product purification and analysis are discussed. W. J. Baker

2922. **Separation of the lanthanons at amalgam cathodes. II. The separation of samarium from gadolinium and purification of europium at a lithium amalgam cathode.** E. I. Onstott (Univ. of California, Los Alamos, New Mexico, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 2070–2076.—Samarium may be efficiently separated from Gd by electrolysis of the citrate complexes at a lithium - mercury cathode or in an acid soln. at pH 5 in the absence of citrate. The dependence of the electrolysis on the cathode potential and electrolyte pH is shown by the data reported, and lithium - mercury is found to be superior to sodium - mercury for the separation. Europium (99·9% purity) can be isolated from mixtures with samarium by careful control of the cathode potential. C. A. Slater

2923. **Spectrographic determination of carbon in sedimentary rocks, using direct-current arc excitation.** W. H. Dennen (M.I.T., Cambridge, Mass., U.S.A.). *Spectrochim. Acta*, 1957, **9** (1), 89–97.—When samples are subjected to cathode excitation at 6 amp. in copper electrodes the carbon present combines with atmospheric nitrogen to form cyanogen, and the band head CN 3883 A is measured. As the nature of the carbon compound, the excitation conditions and the presence of silica cause marked differences in relative intensity it is necessary to compare unknown samples with chemically similar standards, maintaining uniform excitation conditions and diluting samples with quartz. Separate determinations for different compounds of carbon are required. For replicate determinations the coefficient of variation is $\pm$ 13%. K. A. Proctor

2924. **Rapid analysis of carbon monoxide, containing small quantities of oxides of nitrogen, by means of a detector tube.** Yoshitaka Kobayashi (Fac. of Engng, Yokohama Univ., Minami-ku, Yokohama). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1956, **59** (12), 1392–1394.—Since NO and NO_2 interfere with the rapid determination of CO with a detector tube containing $PdSO_4$ and $(NH_4)_2MoO_4$ (Shephard, *Anal. Chem.*, 1947, **19**, 77), their removal was studied with various reagents adsorbed on silica gel. A mixture of CrO_3 and H_2SO_4 was the most satisfactory. Conc. H_2SO_4 (25 ml) and CrO_3 (10 g) are dissolved in water (100 ml), mixed with silica gel (60 to 80 mesh, 100 g) and dried *in vacuo*. The product (0·1 g) is packed in a glass tube (diameter 3 mm). This enables an accurate determination of CO to be made in the presence of 0·05% each of NO and NO_2. K. Saito

2925. **Iodimetric determination of silicon.** R. M. Veĭtsman (All-Union Sci. Res. Inst. of Alloys). *Zavod. Lab.*, 1957, **23** (2), 153–157.—Reduction of the yellow complex of molybdate and silicic acid with KI yields iodine which, after extraction with *iso*butyl alcohol, can be determined colorimetrically or by titration. With samples of titanium dioxide, silicon carbide, tungstic oxide and concentrates, the material is fused with Na_2CO_3 and a portion of the aq. soln. of the melt is just acidified with dil. H_2SO_4. With steel, 1 g is dissolved in 40 ml of dil. H_2SO_4 (1 + 8) and the soln. is heated with 3 g of $(NH_4)_2S_2O_8$ and 20 to 30 ml of water until the Fe is oxidised and the excess of oxidising agent is decomposed. Ethanol (25 ml) is added and the heating is continued until Cr is completely reduced. The soln. is diluted to 100 ml, and 10 ml is mixed with 1 g of H_3BO_3 and treated with 20% NaOH soln. until a ppt. of basic salts forms. Dil. H_2SO_4 (1 + 4) is then added to dissolve the salts, leaving an excess of 0·2 ml. The slightly acid soln. is treated with 3 ml of 10% $(NH_4)_2MoO_4$ soln. and set aside for 5 min. The yellow soln. is mixed with 2 ml of satd. NaH_2PO_4 soln. and after 1 to 2 min. with 10 ml of 20% KI soln. and 5 ml of 10% citric acid soln. The flask is stoppered and set aside in the dark for 15 min. The soln. is then diluted with water to a vol. of 100 to 150 ml and titrated with 0·004 *N* $Na_2S_2O_3$ in the presence of starch. One ml $\equiv$ 0·24 mg of SiO_2. A colorimetric method is also described. G. S. Smith

2926. **Colorimetric determination of silicon in silumin.** V. N. Tolmachev and L. A. Zatuchnaya (Inst. of Chem., State Univ., Kharkov). *Zavod. Lab.*, 1957, **23** (2), 152–153.—The method is based on the colorimetric determination of the molybdenum complex reduced by 1-amino-2-naphthol-4-sulphonic acid. G. S. Smith

2927. **The photometric determination of silicon in high- and medium-percentage ferrosilicon.** E. I Fogel'son and F. S. Kazachkova (I. A. Likhachev Moscow Automobile Works). *Zavod. Lab.*, 1957, **23** (1), 24–25.—The sample (0·05 or 0·1 g) of finely divided (200 mesh) ferrosilicon in an iron crucible is heated for 15 to 20 min. under a cover on a hot-plate with 5 g of dry NaOH. The cooled melt is treated with hot water and then with 200 ml of dil. H_2SO_4 (1:8). The liquid is heated until it becomes clear, then cooled and diluted to 500 ml in a calibrated flask. After further dilution, part of the soln. is taken for photometric determination by the ammonium molybdate - ferrous ammonium sulphate method (Fogel'son, *Anal. Abstr.*, 1956, **3**, 2738). G. S. Smith

2928. **Spectrophotometric studies on organometallic complexes used in analytical chemistry. Germanium complex of 3-hydroxytropolone.** Yoshinaga Oka and Shigeki Matsuo (Inst. of Dressing and Metallurgy, Tohoku Univ., Nagamachi, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1663–1668.—The absorption spectrum of the germanium complex of 3-hydroxytropolone (**I**) was investigated at various pH values. The complex appears to have a molar ratio of Ge to **I** of 1:3.

At pH 7·0, the max. absorption of **I** at 372 mμ is shifted to 387 mμ in the presence of Ge, and Beer's law holds for < 2·0 μg of Ge per ml. At pH 5·5 the absorption of **I** is markedly reduced and the limit of determination of Ge is reduced to 0·05 μg per ml, but the reaction time is increased. K. SAITO

2929. **Determination of a trace amount of copper in germanium oxide with dithizone and neocuproine.** Hideo Baba (The Electrical Communication Lab., Musashino-shi, Tokyo). *Japan Analyst*, 1956, **5** (11), 631–634.—The colorimetric determinations of Cu with dithizone (**I**) and neocuproine (**II**) were compared and it was found that **II** is the more satisfactory reagent. The sample (5 g) is dissolved in redist. HCl (1 + 1, 100 ml) and evaporated almost to dryness. The loss of Cu was examined by the use of radioactive ^{64}Cu; the presence of HNO_3 increases the loss. The residue is dissolved in water (50 ml), mixed with hydroxylamine hydrochloride (10%, 2 ml), Na acetate (30%, 2 ml) (pH 5·6 to 5·8), and 0·1% ethanolic **I** or **II** soln. (2 ml), and extracted with pentanol (30 ml) after 10 min. The organic layer is separated after 20 min. and its extinction measured at 455 mμ. The error is ≃ 25% for 0·14 μg of Cu per g of GeO_2 and ≃ 20% for 0·2 μg of Cu. It was found that the source of Cu in GeO_2 is the water used for the hydrolysis of $GeCl_4$. The water must be distilled three times in a hard-glass still to decrease the content of Cu to < 2 μg per litre. K. SAITO

2930. **Complexometric titrations (chelatometry). XXV. Complexometric determination of tin.** J. Jankovský (Res. Inst. of Ores, Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 373–376.—*Procedure*—Add to the soln. of Sn^{4+} (10 to 50 mg) an excess of 0·05 *M* EDTA (disodium salt), glacial acetic acid (2 ml) and thymol blue, and neutralise dropwise with aq. NH_3 (1:1). Adjust the pH by adding 3 *M* Na acetate (10 ml), dilute to 100 ml, heat to between 70° and 80°, add catechol violet (0·1% aq. soln.) (five drops) and titrate with 0·05 *M* Zn acetate, till the blue colour appears. There is no interference from Ag, Tl, Sb^{V}, Ca, Sr, Ba, Mg, K, Na, Li, ammonium salts, small amounts of Hg^{II} and Be, or from Cl^-, NO_3^-, SO_4^{2-}, Br^-, BO_3^{3-}, ClO_3^- and ClO_4^-; Bi, As, Sb^{III}, WO_4^{2-}, MoO_4^{2-}, Fe^{III}, Ti^{IV}, Al, Mn^{II}, Cr^{III}, Zr^{IV}, phosphates, fluorides, tartrates and oxalates must be absent. In a mixture of Sn with Pb, Cu, Cd, Zn, Ni and Co, one part of the mixture is used for determining the total amount of these elements with the described procedure, and to another part of the mixture are added equal vol. of EDTA (disodium salt) and triethanolamine (**I**). **I** forms a complex with Sn^{IV} and the liberated equiv. amount of EDTA can be titrated with Zn acetate. The difference between the titrations corresponds to the amount of Sn. J. ZÝKA

2931. **Determination of lead in "tinning alloy" of preserving cans.** N. Bruja and V. Dogeanu. *Rev. Chim., Bucharest*, 1956, **7** (9), 546–550.—The small amounts of Pb (≃ 0·04%) in tin removed from preserving cans may be determined by a polarographic method which is not invalidated by small quantities of other ions remaining after pptn. of the bulk of Sn as metastannic acid. A curve has been obtained relating height of the polarographic wave and concn. of Pb in μg per ml by using various proportions of a soln. of Pb acetate and NaOH. The concn. of NaOH is important, since the waves due to Pb become more symmetrical and regular with increasing concn. of alkali. Oxygen is removed by adding Na_2SO_3. H. SHER

2932. **Colorimetric determination of titanium with diantipyrinylmethane.** A. A. Minin. *Uch. Zap. Molotovsk. Univ.*, 1955, **9** (4), 177–181; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,277.—Diantipyrinylmethane (**I**) forms with Ti in acid medium a complex, which in dil. soln. is yellow, and in conc. soln. is orange. To a HCl or H_2SO_4 soln. of Ti add 0·01 g of ascorbic acid (or more if there is a considerable content of Fe), a 5% soln. of $CuSO_4$ (two drops), and 8 to 10 ml of a soln. of **I** in *N* HCl. Dilute to 25 ml with conc. HCl (acidity 5 to 6 *N*) and measure the light absorption with a blue filter. Beer's law is obeyed for ⩾ 30 μg of Ti. Water is used for the comparison. No interference is caused by V, Co, Zn, Cd, Hg, Al, alkali metals, alkaline earths, F^- or PO_4^{3-}. The sensitivity of the method is 20 times greater than that of the H_2O_2 method. C. D. KOPKIN

2933. **Moving plate studies of titanium dioxide.** D. C. Spindler. (Ferro Corp., Cleveland, Ohio, U.S.A.). *Appl. Spectroscopy*, 1957, **11** (1), 28–30.—Variations in optical density of spectral lines during the spark or arc excitation have been studied in order to ascertain the correct exposure conditions for different elements. Of the four methods of plotting discussed, that in which percentage transmittance is plotted against time on two-cycle log paper is illustrated. The ultimate or any convenient line is used. The addition of graphite or copper to test samples is reported. Tungsten is shown to be the best internal standard for titanium determination, and the results suggest that, in general, titanium should be totally burnt. E. G. CUMMINS

2934. **Spectrographic determination of nitrogen and oxygen in titanium.** N. M. Kagan and L. N. Filimonov ('Giprotsvetmetobrabotka' Inst.). *Zavod. Lab.*, 1957, **23** (2), 185–187.—The method described by Sventitskiĭ *et al.* (*Anal. Abstr.*, 1956, **3**, 3596) is found to be unsatisfactory. G. S. SMITH

2935. **Colorimetric determination of zirconium in trace analyses.** M. Pirš. *Rep. J. Stefan Inst., Ljubljana*, 1956, **3**, 175–178 (in English).—Microgram quantities (10 to 40 μg) of Zr are determined by the diminution of colour intensity of a soln. of 4-dimethylaminoazobenzene-4′-arsonic acid after pptn. of Zr. Procedures for determinations in steel, coal ash and bauxite are described: good results were obtained for samples containing up to 0·2% of ZrO_2, with a standard deviation of ±10%. Interference by Ti, Fe, F^-, PO_4^{3-}, WO_4^{2-}, SO_4^{2-}, NO_3^- and molybdate is discussed. O. M. WHITTON

2936. **Determination of zirconium in ores by the iodate method.** Yu. A. Chernikhov and G. I. Kuchmistaya. *Zavod. Lab.*, 1957, **23** (1), 14–18.—Under suitable conditions, Zr can be pptd. by KIO_3 to give amorphous $2Zr(IO_3)_4.KIO_3.8H_2O$ or cryst. $2Zr(IO_3)_4.5KIO_3.HIO_3$, compounds of const. composition which can be used for the iodimetric determination of Zr. The sample (1 g) of ore is treated with 15 ml of HF and 10 ml of dil. H_2SO_4 (1:1) and the soln. is evaporated to fuming. The residue is boiled with 60 to 80 ml of dil. H_2SO_4 or HCl (1:5) together with H_2O_2 to retain Ti, Ta and Nb in soln., and the insol. matter containing the Zr is collected and washed with dil. HCl (1:99)

containing H_2O_2, and then ignited. The residue is fused with 1 to 2 g of KHF_2, the cooled melt is carefully heated with 15 ml of dil. H_2SO_4 and then more strongly to give a pyrosulphate melt which, when cold, is dissolved in 30 to 40 ml of dil. HNO_3 (1:4); 6 to 8 mg of Al^{3+} is added to the clear soln. to act as a collector, followed by NH_4NO_3 (2 g). The ppt. is collected and washed with 2% NH_4NO_3 soln. containing a few drops of aq. NH_3 soln. It is then dissolved in 10 to 20 ml of dil. HNO_3 (1:2), and the cooled soln. is mixed with an equal vol. of a soln. containing 100 g of KIO_3 and 333 ml of conc. HNO_3 in 1 litre of water. The soln. is filtered after 45 to 60 min. if the amorphous ppt. is required or after standing overnight if the cryst. ppt. is required. In either case the ppt. is collected on a glass filtering crucible and washed, first with several 15 to 20-ml portions of a soln. containing 8 g of KIO_3 and 50 ml of conc. HNO_3 in 1 litre of water, and then with 10 to 15-ml portions of 95% ethanol. The washed ppt. is treated with a mixture of 20 ml of dil. HCl (1:4) and 10 ml of 10% KI soln. and the liberated iodine is titrated with 0·1 *N* $Na_2S_2O_3$. Completion of the dissolution of the ppt. occurs during the titration. G. S. SMITH

2937. **Paper-chromatographic separation of zirconium and thorium.** D. Lebez and M. Pirš. *Rep. J. Stefan Inst., Ljubljana*, 1956, **3**, 171–173 (in English).—Satisfactory separation was achieved with acetone - 5% aq. oxalic acid soln. (100:26 to 32) as solvent. The R_F values for each element, and the conditions for optimum separation are specified. O. M. WHITTON

2938. **Volumetric determination of thorium with disodium EDTA—using Fe (II) - cacotheline as indicator.** V. Narayana Rao and G. Gopala Rao (Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1957, **155** (5), 334–336 (in English).—The thorium salt soln. in a buffered soln (pH 2·72) is mixed with cacotheline reagent in an atm. of CO_2 and then with ferrous salt solution, and titrated with Titriplex III (EDTA, disodium salt) until a pink colour appears. Results are accurate within 0·3%. Ferric iron, Zr and phosphates interfere, but ferrous iron does not. W. J. WRIGHT

2939. **Polarographic determination of thorium.** W. G. Krauledat (Dept. of Chemistry, Univ. of Brazil, Rio de Janeiro). *An. Ass. Brasil Quím.*, 1952, [1956], **11**, 147–159.—The polarographic determination of Th is possible with KCl as supporting electrolyte or KNO_3 as complexing electrolyte. The reduction potential varies with the concn. of the complexing electrolyte; this variation is made use of when other compounds can interfere with the determination of Th. When the concn. of Th is small the diffusion current is proportional to concn., but for higher concn. the construction of a calibration curve is recommended because $\frac{i_d}{c}$ is not constant. H. PRITCHARD

2940. **Investigation into the determination of substances in minute quantity. XII. Spectrophotometric determination of minute amounts of thorium and its photometric determination.** Takio Kato, Zenzi Hagiwara and Ichiro Sasaki (Tôhoku Univ., Sendai, Japan). *Technol. Rep. Tôhoku Univ.*, 1956, **21** (1), 15–23 (in English).—Conformity to Beer's law, stability of the complex and gelatin concn. are examined in a proposed method of determination of Th with naphthopurpurin. The Th^{4+} soln. (2 to 30 μg in a max. vol. of 7 ml) is treated with 0·1% gelatin soln. (1 ml) and 0·2% naphthopurpurin soln. (2 ml), and after making up to 10 ml the absorption is measured at 594 mμ. Alternatively, the soln. is titrated photometrically with 0·0025 to 0·005 *M* EDTA (disodium salt). There is no interference from Cl^-, NO_3^-, SCN^- and low concn. of SO_4^{2-}, but $S_2O_3^{2-}$, PO_4^{3-} and F^- cause low results. D. A. PANTONY

2941. **Determination of nitrogen dioxide and nitric oxide in air by a linear-colorimetric method.** E. D. Filyanskaya. *Trudy Nauch. Sess. Vses. Nauch. Inst. Okhranỹ Truda*, 1954, [1955], (1), 205–209; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,319.—The linear-colorimetric method for the determination of gaseous impurities in air is based on the change of colour of a powder in an indicator tube on passing air through. The concn. of the impurity is calculated from the length of the indicator that has changed colour. The indicator carrier is silica gel, containing 38% of water; for determining NO_2 in air, the carrier is saturated with an ethanolic soln. of diphenylamine with NaCl added. The dependence of the length of the coloured column on the concn. of NO_2 in the air has been established. With air containing 0·012 mg of NO_2 per litre, the length of the coloured column is 10 mm in 5 min. To determine NO, the NO is oxidised to NO_2 and its concn. determined by difference. With a concn. of NO_2 or NO plus NO_2 of 0·005 to 0·2 mg per litre, the error of the determination is $\gtrsim$ 10%. C. D. KOPKIN

2942. **Colorimetric method for determination of nitrogen oxides used in (U.S.S.R.) factories manufacturing sulphuric and nitric acids.** R. Petcov. *Rev. Chim., Bucharest*, 1956, **7** (4), 233–238.—The method consists in comparing the colour of the issuing gaseous mixture (NO plus NO_2) with seven standard tubes containing graduated concn. of NO_2 from 0 to 0·3% in steps of 0·05%. Since the oxidation of NO to NO_2 is more rapid the higher the initial concn., the velocity of test gas through the tube must be sufficiently high to enable the initial NO_2 content to be read correctly. Once the initial NO_2 reading is obtained, the inlet valve to the tube is closed, and 10 to 15 min. is allowed for the NO to NO_2 oxidation, when the reading is again taken. H. SHER

2943. **Indole as a reagent for nitrites.** T. K. Zelenova and G. G. Karanovich. *Trudy Vses. Nauch. Inst. Khim. Reaktivov*, 1956, (21), 55–56; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,320.—The reaction between indole and NO_2^- gives the red nitrosoindole. The reaction is carried out in a medium 0·1 to 0·3 *M* in H_2SO_4. To a soln. of the sample of alkali metal or ammonium nitrate in 40 ml of water add a 0·015% soln. of indole (1 ml) and conc. H_2SO_4 (0·75 ml). After 15 min. measure the intensity of the colour with a green filter (520 mμ) or use a series of standards. The colour is stable for 1 hr.; oxidising agents do not interfere. The sensitivity is 0·0003 mg of NO_2^- in 40 ml, with limiting dilution 1 in $13{\cdot}3 \times 10^7$. The error in determining 5 μg of NO_2^- in 3 g of nitrate is $\gtrsim$ 4%. C. D. KOPKIN

2944. **Detection of nitrites and nitrates, alone or combined, in very dilute solutions.** F. A. Steensma (Inst. for Appl. Biol. Res., Natuur-Itbon-T.N.O., Arnhem, Holland). *Chem. Weekbl.*, 1957, **53** (10), 110–111.—A soln. of benzidine in acetic acid gives a yellowish - red coloration with NO_2^-. The yellow

is perceptible at a concn. of 0·0002 mg per ml. Nitrate must be reduced with alkali and zinc dust, treated with acetic acid, and tested as for NO_2^-. A concn. of 0·02 mg per ml can be detected. In tests for NO_2^- and NO_3^- in the presence of each other, if a preliminary test for NO_2^- is positive, the NO_2^- are removed by adding HCl and urea; the soln. is made alkaline and tested for NO_3^-. A low pH strongly reduces the sensitivity of the reaction. Interferences are discussed, and other colorimetric reagents are compared.

W. J. WRIGHT

2945. **The decomposition of nitrous acid under the conditions of polarographic analysis.** J. Mašek (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (1), 51–55.—The removal of HNO_2 by bubbling the soln. prepared for polarographic analysis with an inert gas was studied. The HNO_2 is not only decomposed, but also removed by reason of its volatility. From the stoicheiometry of the decomposition reaction a relation was derived, by use of which the participation of each of these factors in the total removal of HNO_2 can be determined by measuring the height of the hydrogen wave. For the determination of NO_2^- the following conditions are important—the soln. of NO_2^- must not be bubbled with the inert gas after having been acidified; the soln. of NO_2^- must contain not less than a threefold excess of H^+ (HCl, H_2SO_4) as compared with the molar concn. of NO_2^-; the polarographic wave must be recorded immediately after the sample has been prepared. Under these conditions, the wave of NO_2^- ($E_{\frac{1}{2}} = -1{\cdot}0$ V) is suitable for analytical purposes.

J. ZÝKA

2946. **Estimation of sodium hyponitrite in the presence of sodium nitrite, sodium nitrate and sodium carbonate. Action of nitrogen tetroxide or dioxide on hyponitrites.** V. T. Oza (Gujarat Coll., Ahmedabad, India). *Anal. Chem.*, 1957, **29** (3), 452–453.—From 0·01 to 0·1 g of sodium hyponitrite ($Na_2N_2O_2$) can be determined by the reaction between N_2O_4 (0·5 g dissolved in 20 ml of CCl_4 or $CHCl_3$) and $Na_2N_2O_2$ at 0° whereby, after 10 to 15 min., $NaNO_3$ is formed. The liquid is decanted, the residue is washed with solvent and ether, dried at 70°, and dissolved in H_2O, and the NO_3^- are determined by a standard method. No reaction occurs under these conditions with $NaNO_2$, $NaNO_3$ or Na_2CO_3, so that $Na_2N_2O_2$ can be determined in their presence. A suitable assembly for the reaction is shown.

W. J. BAKER

2947. **A spot reaction for phosphorus.** S. Zechner (Luossavaara-Kiirunavaara Aktiebolag, Kiruna C, Sweden). *Mikrochim. Acta*, 1957, (2), 159–160.—A sensitive test for P^V, based on the formation of quinoline molybdophosphate on a filter-paper (7 mm diam.) is described. The detection limit is 1 μg of P^V, and the limiting concn. is 1 in 5×10^4. *Procedure*—Dissolve $Na_2MoO_4.12H_2O$ (10 g) in H_2O (25 ml) and add conc. HCl (11 ml) and conc. HNO_3 (10 ml). Dissolve 1·4 ml of quinoline in a mixture of 15 ml of H_2O, 7 ml of conc. HCl and 6 ml of conc. HNO_3. Mix the two soln. whilst stirring, and add 60 ml of H_2O. The filtered soln. is stable for at least four weeks. Moisten the test paper with the reagent and dry at 60° to 70°. Spot the paper with 0·05 ml of oxidised test soln. which is made 0·1 to 1·6 *M* with HCl or HNO_3. The presence of P^V is indicated by the formation of a bright yellow coloration.

D. F. PHILLIPS

2948. **Colorimetric determination of phosphoric acid with thiourea.** A. M. Meshcheryakov. *Izv. Otd. Estestv. Nauk Akad. Nauk Tadzh.SSR*, 1956, (13), 17–28; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,324.—To determine PO_4^{3-} colorimetrically, add to the soln., containing 0·02 to 0·06 mg of P_2O_5, two or three drops of 2:4-dinitrophenol and 1% H_2SO_4 till the colour disappears. For acid soln., add the indicator, and then 1% alkali to give a pale-yellow colour, followed by acid till the colour disappears. Add 2 ml of molybdate reagent (containing, in 500 ml, 3·762 g of MoO_3 or 4·232 g of H_2MoO_4 dissolved in 75 ml of H_2SO_4, sp.gr. 1·785), 5% thiourea soln. (2 ml), and water to 40 ml. Warm the sample soln. and standard soln. (prepared from KH_2PO_4) containing 0·02 and 0·04 or 0·05 mg of P_2O_5 for 30 min. at 80° to 90° and cool; dilute to 50 ml and measure the extinction.

C. D. KOPKIN

2949. **Investigation into phosphates from the viewpoint of analytical chemistry. III. Qualitative reactions for several phosphates, and some fundamental experiments on the determination of pyrophosphate by the use of hexa-ureachromium chloride.** Takio Kato, Zenzi Hagiwara and Katsu Shiota (Tôhoku Univ., Sendai, Japan). *Technol. Rep. Tôhoku Univ.*, 1956, **21** (1), 1–7 (in English).—The qualitative reactions of several cobalt and nickel ammino compounds and of hexa-ureachromium chloride (**I**) (details of prep. and absorption properties are given) with several phosphates, and the possibility of gravimetric or titrimetric determination of pyrophosphate with **I** are investigated. For quant. analysis, the $P_2O_7^{4-}$ are treated with excess of **I** preferably at 10° and pH 7·50 in a 25% ethanolic soln. The product, $[Cr(CON_2H_4)_6].HP_2O_7.2H_2O$, is dried and weighed, or, after pptn. in hot soln., is treated with hot NaOH and H_2O_2 and the resulting $Cr_2O_7^{2-}$ determined iodimetrically.

IV. Amperometric titration of pyrophosphate by the use of hexa-ureachromium chloride complex as a new reagent. Takio Kato and Zenzi Hagiwara. *Ibid.*, 1956, **21** (1), 9–14.—Preferably, the pyrophosphate is determined amperometrically by titration with **I** in gelatin (0·01%), KCl (0·1 *M*) and ethanol (30 to 35%) soln. under N at $-1{\cdot}3$ to $-1{\cdot}5$ V *vs.* the S.C.E. A precision of $\pm 1\%$ is given.

D. A. PANTONY

2950. **Simple method for the detection of arsenic.** H. Vial de Sachy. *Ann. Falsif.*, 1957, **50**, 53–54.—The dark-brown colour formed on paper impregnated with $CuSO_4$ soln. on exposure to AsH_3 is used as a qual. test; SbH_3 has no effect.

G. H. FOXLEY

2951. **Polarographic determination of arsenic in zinc-smelting residuals and zinc metal.** R. E. Coulson (Imperial Smelting Corp. Ltd., Avonmouth, Bristol, England). *Analyst*, 1957, **82**, 161–164.—In the simple and rapid method described for the determination of 0·1 to 5% of As in residues from the production of Zn from sulphide ores, the sample (10 g) is digested with HNO_3 and then fumed with H_2SO_4. An aliquot (*A*) of the diluted filtered soln. is treated with SO_2, the excess of which is removed by boiling; the cooled liquid is treated with aq. NH_3 until a permanent ppt. of $Fe(OH)_3$ forms and then immediately with 50 ml of 5 *N* H_2SO_4 and 10 ml of 0·25% gelatin soln., and is diluted to 250 ml. A standard soln. of As containing the same concn. of acid and gelatin is prepared, and the polarograms are recorded beginning at

— 0·5 V. If more than 0·1% of Cd is present the aliquot (*A*) is boiled with ferric ammonium sulphate soln. and the Fe is completely pptd. with aq. NH_3. The ppt. which contains the As is collected, washed and dissolved in dil. H_2SO_4, the subsequent procedure being as already described. The absolute accuracies with and without separating the As are ± 0·01 and 0·04%, respectively. An adaptation of the iron-collection method to the determination of As in zinc (down to 0·0001%) is described.
A. O. JONES

2952. **Volumetric estimation of arsenite with potassium permanganate and ceric sulphate. Iodine chloride catalysis in sulphuric acid medium.** K. Bhaskara Rao and G. Gopala Rao (Chem. Dept., Andhra Univ., Waltair, India). *Z. anal. Chem.*, 1957, **155** (3), 161–165 (in English).—Arsenite can be titrated rapidly with $KMnO_4$ to a sharp and stable end-point in *N* H_2SO_4 soln., to which two drops of 0·005 *M* ICl soln. per 50 ml of soln. have been added. The cerimetric estimation of arsenite (and the reverse titration) with ferroin indicator is rapid in H_2SO_4 soln. (< 2 *N*) containing 1 ml of 0·005 *M* ICl soln. per 50 ml of soln. The end-point of the cerimetric estimation can be detected potentiometrically in H_2SO_4 soln. (< *N*) with the addition of 0·5 ml of 0·005 *M* ICl soln. per 50 ml of soln.
J. H. WATON

2953. **Spectrographic determination of micro amounts of arsenic, antimony, bismuth, tin and lead.** Yu Yokoyama (Inst. for Iron, Steel and Other Metals, Tôhoku Univ., Katabiracho, Sendai). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1668–1671.—Calcium nitrate is the best spectrographic buffer for As (> 3 μg), Sb (> 1 μg), Bi (> 0·1 μg), Sn (> 0·3 μg) and Pb (> 0·3 μg), and Cd is the best internal standard. A soln. of the sample in *N* HNO_3 containing $Ca(NO_3)_2$ (3 mg per ml) and $Cd(NO_3)_2$ (0·2 mg per ml) is evaporated, ground to a uniform composition, placed in a crater (diameter 1·5 mm, depth 2 mm) of a carbon electrode (diameter 5 mm, preliminary discharge 6 A, 30 sec.), and arced (120 V, 6 A, 10 sec.). The working curve (Cd 3261·06 *vs.* As 2349·81, Sb 2598·06, Pb 2802·00, Sn 2839·22 or Bi 3067·72 A is linear for 0·1 to 10 μg of Bi, 1 to 100 μg of Sn, Pb and Sb and 10 to 300 μg of As. The standard deviation is < ± 10%, except for Pb (± 16·1%). The presence of Al, PO_4^{3-}, Fe, Na (in an amount greater than half the weight of the Ca), and Mg (greater than one-tenth the weight of the Ca) vitiates the estimation.
K. SAITO

2954. **Detection of a micro amount of vanadium with ion-exchange resins.** Takeo Murase (Ind. Res. Inst. of Aichi Prefecture, Chigusa-ku, Nagoya). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (12), 1826–1833.—A study was made of the use of ion-exchange resins for increasing the sensitivity of the colour reaction of V, and Amberlite IRC-50 (NH_4 form) gave satisfactory results with V oxinate. One drop of the sample soln. on a spot plate is mixed with 2 *N* acetic acid (three drops), a few grains of Amberlite IRC-50 (NH_4 form) and one drop of 0·5% oxine in 2 *N* acetic acid. A pale-green colour develops when V (> 0·03 μg) is present. No interference is caused by the presence of Na, Mg, Ba, Pb, Mn, Zn and PO_4^{3-} (< 800 μg each); Ni and Co decrease the sensitivity to 0·2 μg; whilst Cr, Cu, Al and Ti (> 28 times the weight of the V) interfere. Iron reacts similarly to V. The sensitivity of the reactions of V with H_3PO_4 and Na_2WO_4, and of Fe with 2:2′-dipyridyl was not increased by any resin tested. The green coloration formed in the reaction between diphenylamine and V^V is markedly adsorbed on the resin and increases the sensitivity of detection, but there is interference from various ions.
K. SAITO

2955. **Precipitation of vanadium with phenarsazinic acid.** R. Pietsch (Inst. für anorg. und anal. Chem., Univ., Graz, Austria). *Z. anal. Chem.*, 1957, **155** (3), 189–194.—Between 50 and 60 mg of V, as VO_3^-, in a vol. of 200 ml at pH 2 is quant. pptd. by a threefold excess of phenarsazinic acid (**I**). The ppt. is washed with cold or hot water, dil. acetic acid or cold 0·1 *N* HCl. As the ppt. is not constant in its composition, and since it cannot be ignited to V_2O_5 in the presence of As, the estimation is completed volumetrically. The ppt. is dissolved in 0·5 *N* NaOH and is reduced by boiling with oxalic acid. On weakly acidifying the soln., **I** is pptd., and is filtered off for re-use after drying. The V^{IV} in the filtrate is oxidised with $KMnO_4$ and reduced with Fe^{2+} soln. in the usual way. The use of **I** permits V to be separated from Ni, Mg, Zn and Cr^{VI} and quant. determined, but in the presence of PO_4^{3-}, WO_4^{2-} or MoO_4^{2-} low values are obtained.
J. H. WATON

2956. **Gravimetric determination of vanadic acid as a bismuth salt.** Kazunobu Kodama (Nagoya Municipal Ind. Res. Inst., Rokubancho, Atsuta-ku, Nagoya). *Japan Analyst*, 1956, **5** (11), 628–630.—Vanadate yields a yellowish colloidal ppt. with Bi^{3+} in $HClO_4$, which becomes crystalline on prolonged heating. In HNO_3, HCl or H_2SO_4 soln. appreciable hydrolysis takes place, resulting in high values. The separation from Ag, Pb, Cd, Cu, Fe, Ni, Mn, Al, UO_2^{2+}, Cr and Zr is satisfactory, but the presence of W, As and P vitiates the estimation. The sample soln. (0·3 to 200 mg of V_2O_5) in 0·25 to 0·6 *N* $HClO_4$ is boiled with Bi^{3+} in dil. $HClO_4$ until the ppt. becomes crystalline, then diluted with the same vol. of water and boiled again. The ppt. is filtered off, washed with 2% NH_4NO_3 soln. containing a small amount of HNO_3 and heated at > 675°.
K. SAITO

2957. **Determination of protactinium by gamma spectrometry.** M. L. Salutsky, M. L. Curtis, K. Shaver, A. Elmlinger and R. A. Miller (Mound Lab., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 373–375.—By using a single-channel pulse height analyser (Atom Instr. Co., Model 510) with the subsidiary equipment listed, the concn. of Pa (< 1 p.p.m.) in uranium residues can be estimated from measurements of the gamma pulse height at 300 keV. Interfering isotopes are removed by co-pptn. with thorium fluoride carrier, which leaves the Pa in solution as a fluoride complex. Calibration is carried out with standard soln. of Pa.
E. G. CUMMINS

2958. **Technical measurement of very small and very large concentrations of oxygen in gases.** A. Naumann. *Dechema-Monogr.*, 1956, **27**, 231–244.—Industrial equipment for the determination of < 5% or > 90% of O in gaseous mixtures and in aq. solution is reviewed. There are two main types, involving either (*a*) measurement of a change in a physical property accompanying absorption of the O in a suitable liquid, or (*b*) the paramagnetic properties of O.
A. R. ROGERS

2959. **Sulphur method for determining oxygen (oxides) in metals. II. Determination of micro amounts of oxygen in copper, nickel, chromium and molybdenum.** A. K. Babko, A. I. Volkova and O. F. Drako (Inst. Gen. Inorg. Chem., Acad. Sci., UkrSSR). *Zavod. Lab.*, 1957, **23** (2), 136–140.—The method is based on the reaction of oxides with sulphur vapour (*Anal. Abstr.*, 1956, **3**, 3611), but *in vacuo* instead of in an atmosphere of N, since in the latter case some combination of N and S occurs and the subsequent passage into water yields SO_2 and NH_3 from this source. The SO_2 obtained in the reaction of S with the oxides in the metal is determined colorimetrically with the fuchsine - formaldehyde reagent. The apparatus used is described.
G. S. SMITH

2960. **Potentiometric and volumetric estimation of peroxides with alkaline permanganate.** I. M. Issa and H. Khalifa (Fac. of Science, Cairo Univ., Egypt). *J. Indian Chem. Soc.*, 1956, **33** (11), 778–780.—The potentiometric method is based on the reduction of alkaline $KMnO_4$, in the presence of telluric acid, to Mn^{4+}. In the volumetric method, the peroxide soln. is mixed with excess of $KMnO_4$ in the presence of 0·5 *N* NaOH and 0·2 g of telluric acid, and the excess of $KMnO_4$ is determined with oxalic acid or Fe^{2+}. The errors, in either method, differ from the acid $KMnO_4$ method by $\gtrless$ 0·5%.
I. JONES

2961. **Direct colorimetric determination of elementary sulphur.** H. A. Ory, V. L. Warren and H. B. Williams (Coastal Studies Inst., Louisiana State Univ., Baton Rouge, U.S.A.). *Analyst*, 1957, **82**, 189–192.—The Schoenberg reagent, N-(4:4′-dimethoxybenzohydrylidene)benzylamine, provides a direct colorimetric quant. test for free S. The reaction was studied by means of infra-red spectroscopy. Phenyl cyanide was shown to be one of the products of the reaction, which proceeds through a series of possible intermediates. The sample (containing milligram amounts of free S) is mixed with 15 times its weight of the reagent, and the mixture is heated in a small test-tube at 210° for 10 min. The cooled product is extracted with benzene until no more blue colour is extracted. The filtered extract is adjusted to 25 ml and its extinction is measured at 590 mμ. Standard graphs are made from standard soln. of S in CS_2 which are evaporated to dryness and the residue submitted to the procedure described. The accuracy of the method is within 3%. The mechanism of the reaction is discussed.
A. O. JONES

2962. **Sulphur estimation in sulphide ores by use of EDTA (disodium salt).** J. Doležal, Z. Šulcek and J. Soták (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Průmysl*, 1957, **7** (2), 63–65.—A rapid method has been worked out for pyrites of different kinds and types; for pyrrhotite, chalcopyrites, sphalerite, galena and their concentrates. Interfering metals (Fe, Al, Cr, Cu, etc.) can be removed with EDTA. *Procedure*—To a finely pulverised sample (1 g) add inverse aqua regia (10 ml) and a few drops of Br. After decomposition evaporate to dryness, add HCl (1 ml) and after 5 min. add hot water (50 ml). The pptd. SiO_2 is filtered off and diluted to 250 ml. To 50 ml of the soln. add acetate buffer (20 ml), 0·1 *M* EDTA (20 ml) and hot water (200 ml). Heat to boiling and precipitate with 0·05 *M* $BaCl_2$ ($\simeq$ 25 ml). After heating for 2 hr. on water bath the ppt. is filtered off and washed with hot water (300 ml), dried and heated at 600°.
J. BÖSWART

2963. **Titrimetric determination of sulphate with lead nitrate as titrant and dithizone as indicator.** E. E. Archer (The Distillers Co. Ltd., Great Burgh, Epsom, England). *Analyst*, 1957, **82**, 208–209.—The soln. containing 0·2 to 0·4 milli-equiv. of SO_4^{2-} is diluted to 10 ml and neutralised to bromophenol blue with aq. NH_3 or dil. HNO_3. It is then treated with acetic acid (20%, v/v) (1 ml), acetone (50 ml) and freshly prepared dithizone soln. (1% in acetone) (1 ml), and titrated with 0·02 *N* $Pb(NO_3)_2$ soln. until the colour changes from green to purple. When traces of metals that react with dithizone are present, sufficient dithizone is added to render the soln. blue - green. The liquid is then titrated as before, but the end-point is less sharp and the accuracy moderate. If considerable amounts of reactive metals are present they are removed by means of an ion-exchange resin. For the determination of S in organic compounds, the sample is oxidised with fuming HNO_3 at 280° for 3 hr. The digest is evaporated to dryness with aq. NH_3 and the evaporation is repeated after addition of water. The residue is dissolved in water (10 ml) and is treated as already described. When Cl^- are present, the soln. is evaporated to dryness with an excess of HNO_3. Sufficient ammonium or alkali-metal ions must be present to retain the SO_4^{2-}.
A. O. JONES

2964. **Determination of milligram amounts of thiosulphate by a clock reaction.** J. B. Risk and J. D. H. Strickland (Brit. Columbia Res. Council, Vancouver, Canada). *Anal. Chem.*, 1957, **29** (3), 434–437.—Concn. of 10^{-5} to 10^{-4} *M* of $S_2O_3^{2-}$ delay the oxidation of *p*-phenylenediamine ($\simeq 10^{-3}$ *M*) by $FeCl_3$ ($\simeq 10^{-3}$ *M*) at 25°; the colour (violet if S^{2-} are present, orange if absent) appears rapidly after an induction period (1 to 30 min.) that is proportional to the concn. of $S_2O_3^{2-}$. This specific chronometric reaction can be used to determine from 0·25 to 0·5 mg of $S_2O_3^{2-}$ in the presence of S^{2-}, SO_3^{2-} or SO_4^{2-}, *e.g.*, in a 0·5-ml sample of sulphate-pulp "black liquor." The end-point can be recorded to within 1 sec. and the max. accuracy is within $\simeq \pm 1\%$. Interferences are discussed.
W. J. BAKER

2965. **Determination of sulphate in chromium-plating solutions.** C. J. Keattch (British Non-Ferrous Metals Res. Ass., Euston Rd., London). *Electroplating*, 1957, **10** (1), 2–6.—A method and apparatus are described. The method is based on the quant. reduction of sulphate to sulphide by a mixture of hydriodic, hypophosphorous and hydrochloric acids. The H_2S liberated is absorbed in NaOH and the determination finished by the usual iodine - thiosulphate titration.
S.C.I. ABSTR.

2966. **Polarographic analysis of chromate pigments.** J. Baltes and P. Wiertz (Res. Inst. for Fatty Materials, Munster, Westphalia, Germany). *Peint-Pigm.-Vern.*, 1957, **33** (3), 222–225.—Lead or zinc chromate pigments are analysed for Pb^{2+} or Zn^{2+} and CrO_4^{2-} in a single operation by dissolving the pigment in aq. KOH and diluting an aliquot with a buffer soln. containing NH_4Cl, ammonium citrate and NaOH in equimolar proportions. The polarogram is then determined with a dropping-mercury electrode, and the metal contents are calculated with reference to standard calibration curves.
L. A. O'NEILL

2967. **X-ray absorption edge spectrometry as an analytical tool. Determination of molybdenum and zinc.** R. E. Barieau (California Res. Corp., Richmond, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 348–352.—This scheme of analysis, based on the discontinuity in the X-ray mass absorption coefficient at an edge, is known to have no matrix effect and is therefore preferable at high concentrations to X-ray fluorescence. Calibration and equations and methods of measurement are presented for the determination of Mo and Zn in liquid hydrocarbons. Other successful determinations include Pb and Br in engine combustion chamber deposits, and Mo, Ni and Pt in solids. The apparatus consists of a copper target X-ray tube source plus a converted modern X-ray diffractometer, with an argon-filled chlorine-quenched Geiger tube detector. The results are compared and contrasted with those of the emission spectrograph, and recent instrumental improvements are noted.
E. G. CUMMINS

2968. **Determination of uranium by ammonium thiosulphate and sodium hypophosphite.** H. N. Rây and N. P. Bhattacharayya (Indian Ordnance Dept., Ichapore, W. Bengal, India). *Analyst*, 1957, **82**, 164–166.—Uranium is determined gravimetrically by pptn. as the greenish phosphate formed when a soln. in dil. mineral acid is boiled with NaH_2PO_2 and then treated with $(NH_4)_2S_2O_3$ soln. The collected ppt. is washed with dil. HCl (1%) and then with hot water until free from Cl^-, and is finally ignited, first at low temp. and then at 900°. Analysis of the ppt. prepared from pure materials indicated the composition $UO_2P_2O_7$ (53·60% of U). The reaction occurs only with U^{6+}. Elements forming insol. sulphides are removed by preliminary treatment with H_2S; Zr and Ti, the only other interfering elements, are removed by boiling the soln. with NaH_2PO_2 alone. A slightly modified procedure for the determination of U in steel is described.
A. O. JONES

2969. **Rapid routine method for determination of uranium in ores.** H. J. Seim, R. J. Morris and D. W. Frew (The Univ., Reno, Nev., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 443–446.—The soln. from the acid decomposition of the sample ($\equiv$ 0·5 to 40 mg of U) is adjusted to pH 1 to 1·5 with 6 *M* NaOH, and any Fe and/or V present is reduced with aq. 6% H_2SO_3. The soln. is then passed through a column (50 mm × 10 mm) of Amberlite XE-117, Type 2, at a rate of one drop per sec., whereby only the uranyl sulphate complex is adsorbed (*cf.* Fisher and Kunin, *Anal. Abstr.*, 1957, **4**, 2970). The U is eluted with boiling *M* $HClO_4$ (one drop per sec.) and determined spectrophotometrically at 380 mμ (for low concn.) or 420 mμ (for high concn.) by using the NaOH - H_2O_2 procedure (Fisher, *Rep. U.S. Atomic Energy Comm., Document* RMO-2530 and -2531, 1954). Interference from $>$ 250 mg of Fe combined with $>$ 250 mg of P_2O_5 is eliminated by a simple filtration. Concn. as low as 0·01% of U_3O_8 can be determined to within ±0·005%; $\simeq$ 20 analyses can be made per operator per day.
W. J. BAKER

2970. **Use of ion-exchange resins for determination of uranium in ores and solutions.** S. Fisher and R. Kunin (Rohm & Haas Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 400–402.—A complete separation of U^{6+} from interfering ions can be made by adsorption of the sulphate complex of U^{VI} on a quaternary ammonium anion-exchange resin (Amberlite XE-117, Type 2, sulphate form) in a tube (0·5-in. diam.) with a 5- or 10-ml bed. Interference by Fe^{3+} and V^{5+} is avoided by a preliminary reduction of the sample soln. (50 ml) with 6% H_2SO_3, so that they and all other cations pass through the column. The flow rate should not exceed 2 ml per min. The U is eluted from the column with 50 ml of *M* $HClO_4$, and is then determined colorimetrically or volumetrically. A soln. of the ore ($\equiv <$ 100 mg of U) is obtained preferably by digestion with 20% H_2SO_4 (20 ml) and MnO_2 (2 g) at 100°, followed by dilution, when cool, to 50 ml (pH 1·0 to 1·5) and filtration. If the ore is decomposed with 12 *M* HCl plus 16 *M* HNO_3, followed by fuming with H_2SO_4, the final soln. should not be stronger than 0·1 *M* in Cl^- or 0·01 *M* in NO_3^-, otherwise some U will pass into the first (sample) eluate. For uranium leachates the accuracy is within ± 2%; for ores the accuracy is satisfactory but it depends on the dissolution procedure used.
W. J. BAKER

2971. **Remote-control determination of corrosion products and additives in homogeneous reactor fuel. Application of ion exchange.** A. D. Horton, P. F. Thomason and M. T. Kelley (Oak Ridge Nat. Lab., Tenn., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 388–391.—Apparatus is described and general procedures are outlined for the separation and determination of Al, Ni, Fe, Mn, Zn, Cu, Cr, Zr and Co (each in concn. $\lessapprox$ 5 to 20 μg per ml) in $UO_2(SO_4)_3$ soln. from the reactor. In most instances, the metal is adsorbed from 4·5 or 9 *M* HCl, or dil. H_2SO_4, on to a suitable anion- or cation-exchange resin. After elution of the column with HCl, H_2O or H_2SO_4, the eluate containing the metal is collected in a calibrated polarographic-cell sample-holder, evaporated to dryness, redissolved and diluted to 5 or 10 ml with the proper supporting electrolyte for polarography. Aluminium and Zr are determined, in $\simeq$ 50 ml of eluate, spectrophotometrically at 525 and 555 mμ, respectively. Copper is determined by direct polarography of the sample ($\gtrsim$ 1 ml) to which is added 2·5 ml of 0·5 *M* EDTA (disodium salt) and H_2O to make 5 ml. The standard deviation for each metal varies from 0·7 to 3·2% (four analyses).
W. J. BAKER

2972. **Determination of ionium.** I. E. Starik, A. S. Starik, G. S. Lozhkina and L. V. Talitskaya. *Byull. Komiss. Opredel. Absolyut. Vozrasta Geol. Formats., Akad. Nauk, SSSR*, 1955, (1), 47–52; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1234.—In HNO_3 soln., the isotopes of Th are removed as oxalates on Ce as carrier. Then Ra-D, Ra-E and Po are removed by electrolysis in *N* HNO_3 at 100 milliamp. for 9 hr. at 2·1 V. As indicator for determining the completeness of the separation of Io, UX_1 is used. It is established that (*i*) a double pptn. of Ce and Io oxalates completely frees them from Ra and U; (*ii*) the doubly pptd. Ce oxalate adsorbs 7 to 12% of Po, $>$ 30% of Ra-E and 2 to 3% of Ra-D; (*iii*) on separating Ce and Io from Ra-D, Ra-E and Ra-F with H_2S, complete separation is effected from these elements, but 30% of the Io is adsorbed by the sulphide ppt.
C. D. KOPKIN

2973. **Spectrophotometric determination of fluoride. I. Zirconium - sodium purpurinsulphonate lake method.** Saburo Wakimoto (Hygiene Lab., Fukuoka Prefecture, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (10), 1489–1492.—The Na purpurinsulphonate (**I**) lake of Zr

(max. absorption 520 mμ) decomposes on addition of F^- in > *N* HCl soln. **I** has max. absorption at 490 mμ, and the amount of F^- (> 0·02 p.p.m.) is calculated from the decrease in extinction at 520 mμ. The working curve is linear for < 120 μg of F^- in 100 ml. The sample soln. (50 ml) is mixed with the lake soln. (10 ml) [prepared by mixing equal vol. of **I** (0·13 g in 1 litre) and Zr soln. (0·12 g of $Zr(NO_3)_4$ dissolved in 5 ml of conc. HCl and 100 ml of water and diluted with dil. HCl to produce 1 litre of 2·4 *N* HCl)] and set aside for 30 min.; the extinction should then be measured within 3 hr. The presence of SO_4^{2-} (> 100 p.p.m.) and PO_4^{3-} (> 0·80 p.p.m. for < 0·80 p.p.m. of F^-) vitiates the estimation. This method is applicable to the determination of F^- in a hot spring or an underground water.

K. SAITO

2974. **Determination of chlorides and bromides by chronometric titration.** E. K. Nikitin and E. N. Ponomareva. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10) 234–245; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1258.—The chronometric titration method consists in the determination of the initial point of the reaction, fixed by the fall of one drop of a sulphite soln. into a tube containing the soln. to be analysed, and the end-point of the period of induction, determined by the sudden appearance of the starch - iodine colour after all the SO_3^{2-} have been oxidised. To determine Br^-, mix 5 ml of a 0·001 *M* soln. of $K_2S_2O_5$ with 5 ml of the sample soln. and 1 ml of 0·5% starch soln. Add from a burette one drop of a mixture of 0·1 *M* H_2SO_4 and 0·2 *M* KIO_3 (1:1). In determining Cl^-, the concn. of iodate is increased 10 times, while that of the acid is increased 20 to 25 times. A control experiment is carried out without the indicator, by adding to 10 ml of 0·1 *N* HCl that vol. of 0·1 *N* KOH or NaOH which is necessary to neutralise 10 ml of the acid to phenolphthalein, and making up to 100 ml. The control soln. of Br^- is made up in the same way, or by dissolving a known wt. of pure salt. The concn. of Cl^- is found from the formula $c_x = c[t_c(t_o - t_x)]/[t_x(t_o - t_c)]$, where c_x and c are the concn. of the sample and standard soln., t_x and t_c are the periods of induction of these soln., and t_o is the period of induction for the control experiment. The error in the determination of Cl^- is ≯ ± 2·6%.

C. D. KOPKIN

2975. **Method for the detection and determination of iodide in the presence of chloride.** M. Z. Barakat, M. F. Abd El-Wahab and M. M. El-Sadr (Biochem. Dept., Faculty of Medicine, Abbassia, Ein-Shams Univ., Cairo, Egypt). *Analyst*, 1957, **82**, 192–196.—The bismuth - 2-mercaptothiazoline reagent (prep. described) reacts with I^- to give an intensely red insol. complex iodide, which is sol. in excess of the iodide but not in excess of the reagent. There is no reaction with F^-, Cl^-, ClO_3^- or ClO_4^-; Br^- give a yellow ppt. (sol. in excess of the test soln.), but in the presence of I^- the red colour predominates. Interference occurs with NO_2^-, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, IO_3^-, IO_4^-, BrO_3^- and CrO_4^{2-}, but other common acid radicals do not interfere. For the gravimetric determination of I^-, an aliquot of the soln. is treated with excess of the reagent, the ppt. is collected on asbestos or paper in a tared Gooch crucible, washed with the reagent soln., water and finally with ethanol, and dried *in vacuo* over H_2SO_4. Results are based on the formula $C_4H_{10}N_2I_2S_4Bi$. No modification of the procedure is necessary in the presence of Cl^-. The error does not exceed 0·6%. The use of antimony - 2 - mercaptothiazoline for the detection of I^- in the presence of the other halide ions is also described.

A. O. JONES

2976. **The determination of manganese with sodium bismuthate. II. Simultaneous colorimetric determination of chromium and manganese in mixtures.** Hisashi Kiyota and Toshio Yamamoto (Chem. Dept., Kyoto Gakugei Univ., Kita-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1746–1749.—Experimental conditions for the colorimetric determination of Cr (< 50 μg per ml) and Mn (< 50 μg per ml) with sodium bismuthate were studied. The sample soln. is made 3 *N* with H_2SO_4 and heated with $AgNO_3$ (10%, three drops) and sodium bismuthate (0·3 g) at 40° for 30 min. The extinction is measured at 550 mμ for the determination of Mn, and then at 365 mμ, the Cr being calculated from an empirical formula.

III. A modification of the detection and volumetric determination of manganese. Hisashi Kiyota and Toshio Yamamoto. *Ibid.*, 1956, **77** (11), 1749–1751.—For the vol. determination of Mn (< 15 mg), a 10 *N* H_2SO_4 soln. of the sample is heated with a few drops of 10% $AgNO_3$ and $NaBiO_3$ (< 0·5 g) at 40° for 20 min. The excess of $NaBiO_3$ is thus decomposed, and the product is treated with $Fe(NH_4)_2(SO_4)_2$ soln. without filtration.

K. SAITO

2977. **Separation of rhenium from vanadium and tungsten by ion-exchange chromatography.** D. I. Ryabchikov and A. I. Lazarev. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 64–76; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1236.—To remove Re from V, pass 100 ml of 0·3 *N* HCl containing ≯ 75 mg of V through a column of 10 g of anionite MMG-1 (OH form) at a rate of ≯ 3 ml per min. On washing the column with 100 ml of 0·3 *N* HCl, V passes into the eluate; the Re retained by the anionite is washed out with 250 ml of 2·5 *N* NaOH. The separation may also be carried out on cationite SBS (H form). Pass 100 ml of the soln., acid to Congo red, through a column containing 15 g of cationite at 2 to 3 ml per min. Wash with 150 ml of acidified water; Re passes into the eluate as ReO_4^-; V is eluted with 100 ml of aq. NH_3 (1:4). To separate V and W, add to 50 ml of a soln. of W^{VI} and V^V 2·5 ml of 3% H_2O_2 and HCl to a pH of 1·0. Pass the coloured soln. through a column of an ion-exchange alumina. The V may then be separated by washing with 25 ml of a soln. of pH 1·0, containing 1 ml of 3% H_2O_2, and with 75 ml of HCl soln. of pH 1·0 without H_2O_2. The W may then be removed from the column with 200 ml of 25% aq. NH_3 soln. To remove Re from W, fuse 0·05 to 0·15 g of sample in a platinum crucible with 3 g of Na_2CO_3 and 0·5 g of $NaClO_3$. Cool, and leach with hot water. Neutralise the soln., containing Na_2WO_4, $NaReO_4$, $NaCO_3$ and NaCl, with HCl to Congo red and pass through a column of anion-exchange alumina previously washed with 20 ml of 0·1 *N* HCl. The Re is washed out with 75 ml of 0·1 *N* HCl. Dilute the eluate and wash liquors to 200 ml, and to 25 or 30 ml add 10 ml of HCl (sp.gr. 1·19), cool and add 20% NH_4SCN soln. and 1·5 ml of a 25% soln. of $SnCl_2$ in HCl (1:1). Dilute to 50 ml and after 10 min. determine the rhenium thiocyanate complex visually or photometrically. Wash out W from the column with 200 ml of aq. NH_3 (1:3) and 50 ml of water. To the eluate add 50 ml of conc. HCl and 10 ml of a 0·5% soln. of gelatin, and set aside for 40 to 60 min. on the water bath. Filter and wash the ppt. with hot HCl

(× 5). Burn off the filter-paper and ignite the ppt. at 700° to 800° to WO_3. C. D. KOPKIN

2978. **The photometric micro-determination of iron with ferron and tributylammonium salts.** M. Ziegler, O. Glemser and N. Petri (Anorg. Chem. Inst., Univ. Göttingen, Germany). *Mikrochim. Acta*, 1957, (2), 215–224.—A rapid method for the determination of 0·1 μg of Fe is described which is based on the reaction between Fe^{3+}, ferron and tributylammonium acetate with formation of a green compound. This product is water-sol. and can be extracted with various organic compounds. No interference is experienced in the presence of a 5×10^5 excess of other transition elements. The procedure is applicable to the testing of numerous salts and especially alkali phosphates. The determination of 0·5% of Fe in pure aluminium can be carried out on only 0·1 mg of sample, so that the homogeneity of aluminium-base materials may be investigated by using the method.

D. F. PHILLIPS

2979. **Method for the accurate estimation of iron and of oxidising agents.** W. Kangro and H. Pieper (Inst. für Chem. Metall., Tech. Hochsch., Braunschweig, Germany). *Z. anal. Chem.*, 1957, **155** (3), 169–183.—The determination of Fe by the internal electrolysis of ferric halides between platinum and silver electrodes described by Kangro and Wiebke (*Arch. Eisenhüttenw.*, 1954, **25**, 327) gives errors of $\simeq +$ 0·01%. When adapted to the determination of iodine in KI soln. (1 mole : 5 moles), the errors are $\simeq +$ 0·02%. Other oxidising agents give somewhat high values, but these are constant and are reproducible to within $\pm$ 0·02%. A simplified procedure is described for the determination of Fe, which yields errors of $\simeq -$0·07%; the method is valid in the presence of Zn, Al or Ni.

J. H. WATON

2980. **Rapid determination of iron in products of the cobalt industry by means of extraction.** L. M. Gindin and É. F. Kouba (Norilsk Mining-Metallurgy Combine). *Zavod. Lab.*, 1957, **23** (2), 150–151.—The soln. (20 ml) of cobalt salts is mixed with 30 ml of conc. HCl in a separating funnel and shaken for 15 to 20 sec. with 25 ml of *iso*amyl acetate. The solvent layer containing the Fe is shaken with 25 ml of water, which extracts the Fe. Iron is determined colorimetrically with sulphosalicylic acid against an artificial scale of standards containing $FeCl_3$, $CoSO_4$ and HCl. With high contents of Co, several extractions may be necessary.

G. S. SMITH

2981. **Depolarisation on the dropping-mercury electrode by suspensions of insoluble matter. II. Suspensions of bivalent iron, cobalt and nickel sulphides.** K. Micka (Polarogr. Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 233–242.—By studying the polarographic behaviour of aq. suspensions and colloidal soln. of FeS, NiS and CoS, it has been shown that the suspension yields a catalytic current on the dropping-mercury electrode, indicated by a sharp max. (− 1·5 to − 1·7 V *vs.* the S.C.E.). The magnitude of the current depends on the time elapsed since the preparation of the suspension. The time elapsed between the formation of the sol and the origin of the catalytic current has been defined as the coagulation time, and this is said to increase with the stability of the sol. The observed effects are not quite clear from the theoretical point of view, but are of practical importance, *e.g.*, in polarographic titrations, when the presence of suspensions can cause interference. J. ZÝKA

2982. **Amperometric titration of ferrocyanide.** Zenzi Hagiwara (Tôhoku Univ., Sendai, Japan). *Technol. Rep. Tôhoku Univ.*, 1956, **21** (1), 25–29 (in English).—Ferrocyanide (42·4 mg per 20 ml) is titrated amperometrically at −1·0 to −1·3 V *vs.* the S.C.E. with 0·06 *M* hexa-ureachromium chloride in the presence of gelatin and KCl under N. Reproducibility data are presented, and evidence for the formula of the product, $[Cr(CON_2H_4)_6]_4[Fe(CN)_6]_3$, is given. D. A. PANTONY

2983. **The use of an air jet in the spectrographic analysis of low alloy steel.** D. L. Fry and T. P. Schreiber (General Motors Corp., Detroit, Mich., U.S.A.). *Appl. Spectroscopy*, 1957, **11** (1), 1–6.—The effect of an air jet, velocity 1500 ft. per min., blown through the analytical gap (⅛ in. diam.), has been investigated. Non-self-reversing lines were measured, using an air-interrupted-type source with five different sets of conditions, all listed. Each source condition gave similar reproducible curves for an element without an air jet. Tests on samples of different sizes but identical composition showed that, with an air jet and point-to-plane technique, differences due to standard-to-sample size variation are reduced. The effect of an air blast on intensity variation due to heat treatment is discussed. The small translational shift effect of an air jet on the standard curves is illustrated by graphs. It is concluded that an air jet is an advantage only when submitted samples differ in history, physical size, or chemical composition from routine.

E. G. CUMMINS

2984. **Colorimetric determination of silicon in steel by ion exchange.** Ya. A. Degtyarenko and V. V. Oshchapovskiĭ. *Nauch. Zap. L'vovsk. Politekhn. Inst.*, 1956, (22), 107–110; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1245.—To 0·1 g of the steel add 7 ml of HNO_3 (1 : 1), 7 ml of HCl (1 : 1) and warm. Dilute to 250 ml, filter, and pass 5 or 10 ml through a column of cationite at a rate of 2 to 3 ml per min. Wash the column with H_2O (5 × 5 ml). The time of filtration and washing is $\gtrsim$ 5 to 7 min. Collect the filtrate and wash liquors in a 50-ml flask, add 1 ml of 5 *N* H_2SO_4 and 3 ml of a 5% soln. of ammonium molybdate. Mix and allow to stand for 10 min. Add 4 ml of 8 *N* H_2SO_4, followed by the dropwise addition of 3 ml of a 0·5% soln. of $SnCl_2$. Make up to the mark, mix, and after 5 min. measure the intensity of the colour. A standard soln. is prepared by solution of a sample of Na_2SiF_6. C. D. KOPKIN

2985. **The spectrographic determination of iron and magnesium in aluminosilicates.** S. N. Aleksandrov, Ya. E. Shmulyakovskiĭ and G. P. Malakhova. *Khim. i Tekhnol. Topliva*, 1956, (6), 55–57; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1238.—The method has been worked out for the concn. range 0·04 to 1% of Fe_2O_3 and 0·1 to 1% of MgO. The pairs of lines used are Fe 2585 - Si 2532 A, and Mg 2776 - Si 2532 A. The powdered samples are mixed with $BaCO_3$ in the proportion 1 : 3, and placed in a crater in the carbon electrode. The error is 10%. The standards are prepared by adding compounds of Fe and Mg to a pure washed aluminosilicate, followed by ignition and grinding, and constructing graphs from the results.

C. D. KOPKIN

2986. **Determination of titanium nitride in steel.** Yu. A. Klyachko and M. M. Shapiro (Centr. Sci. Res. Inst. of Ferrous Metallurgy). *Zavod. Lab.*, 1957, **23** (2), 140–143.—The sample of steel (6 to 7 g) is decomposed electrolytically in a soln. containing 15% of NaCl and 2·5% of tartaric acid at a c.d. of 0·7 amp. per sq. cm. The insol. matter is washed and dissolved in a mixture of 16 ml of H_3PO_4 (sp.gr. 1·83), 6 ml of conc. H_2SO_4, 2 g of $KHSO_4$ and 5 ml of 20% $K_2Cr_2O_7$ soln. The N is then determined by the usual distillation process.
G. S. SMITH

2987. **Colorimetric determination of molybdenum in steel by means of extraction.** F. G. Zharovskiĭ and É. F. Gavrilova (T. G. Shevchenko Kiev State Univ.). *Zavod. Lab.*, 1957, **23** (2), 143–146.—The neutral soln. (10 to 12 ml) containing Mo, and 8 ml of phenylhydrazine soln. (concn. not stated) acidified with H_2SO_4 are heated for 15 min. on a sand bath. The cooled soln. is diluted to 50 ml in a calibrated flask and 10 ml is extracted with 5-ml amounts of *iso*amyl alcohol until the last extract is colourless. The combined extracts are diluted with *iso*amyl alcohol to 25 ml in a calibrated flask and the extinction is measured on a photo-electric colorimeter with a green filter. The content of Mo is found from a calibration curve. The method of obtaining the soln. from a sample of steel is not described. Tungsten does not interfere.
G. S. SMITH

2988. **Rapid determination of nickel by an extraction method.** L. M. Gindin and É. F. Kouba (Norilsk Mining Metallurgy Combine). *Zavod. Lab.*, 1957, **23** (1), 19–20.—An application of the $CHCl_3$ extraction method for separating the dimethylglyoxime compounds of Ni and Co is described. Treatment of the extract containing the Ni with aq. NH_3 soln. removes any remaining Co.
G. S. SMITH

2989. **3-Hydroxy-1-*p*-sulphonato[sulpho]phenyl-3-phenyltriazine as a colorimetric reagent for palladium.** N. C. Sogani and S. C. Bhattacharyya (Nat. Chem. Lab., Poona, India). *Anal. Chem.*, 1957, **29** (3), 397–400.—A 0·1% (w/v) aq. soln. of the reagent can be used for the detection and determination of 0·2 to 6 p.p.m. of Pd in dil. HNO_3 soln. (pH 1·7 to 4·4). The sol. coloured palladium complex forms immediately and is stable for 24 hr. between 25° and 85°. The reagent is highly selective; there is no interference from Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Ag^{+}, Pt^{4+}, Rh^{4+}, Ir^{3+} or Ru^{3+}. The sensitivity is 1 in 20×10^6, of 0·05 μg of Pd in 0·15 ml of soln. on a spot-plate. Beer's law is valid, whilst the reagent and complex have well-separated absorption peaks so that a spectrophotometric determination of Pd can be made at 420 mμ (0·2 to 5 p.p.m., with the reagent as blank), 430 mμ (0·4 to 6 p.p.m., with H_2O as blank) or 435 to 450 mμ (for larger amounts of Pd). The prep. of the reagent is described.
W. J. BAKER

2990. **Spectrographic analysis of ores by the introduction of powders into the arc discharge by means of air.** A. K. Rusanov and V. G. Khitrov (All-Union Inst. of Mineral Raw Materials). *Zavod. Lab.*, 1957, **23** (2), 175–184.—The method previously described (*Anal. Abstr.*, 1956, **3**, 1561) is studied in greater detail in application to the determination of a large number of elements. The increased degree of sensitivity and reproducibility is confirmed. It is suggested that the method is suitable for automatic spectrographic analysis.
G. S. SMITH

2991. **Quantitative infra-red analysis of apatite mixtures.** R. B. Fischer and C. E. Ring (Indiana Univ., Bloomington, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 431–434.—By using a calibration curve built up from the potassium iodide disc spectra in the "KBr region" of apatite mixtures, based on the 17·5-μ and the 17·8-μ bands of fluorapatite and hydroxyapatite, respectively, the measurement of one in the presence of the other has been achieved. The two possible methods of calibration considered, a base-line technique and an area-measurement method, specially for analyses in which calcium fluoride is present, are discussed. They give average errors of 1·5% and 1·2% of fluorapatite in the sample, respectively.
E. G. CUMMINS

See also Abstracts 2865, 2866, 2867, 2869, 2870, 2871, 2872, 3010, 3036, 3037, 3202.

3.—ORGANIC ANALYSIS

2992. **Determination of carbon, hydrogen and fluorine in organic compounds.** L. Mázor (Inst. für allgemeine Chemie, Tech. Univ., Budapest, Hungary). *Mikrochim. Acta*, 1957, (1), 113–124.—A slightly modified conventional combustion tube is used in a method designed for the simultaneous determination of C, H and F. Lead oxide is used to combine with the HF and as the oxidant. A thin alundum tube coated on the inside with Pb_3O_4 is inserted in the empty glass combustion tube, and the combustion products, after passing through a platinum spiral, are passed through the tube which is heated to between 550° and 570°. Carbon and hydrogen are oxidised and are determined in the conventional manner by using $Mg(ClO_4)_2$ and ascarite. Fluorine forms PbF_2 which is dissolved and is determined gravimetrically as lead chlorofluoride. Results are given for several solid and volatile fluorine-containing compounds.
P. S. STROSS

2993. **Organic micro-analysis. XII. The rate of generation of oxygen from several metal oxides used for the combustion of the sample in the Dumas nitrogen determination.** Keiichiro Hozumi and Shigeo Kinoshita (Pharm. Dept., Med. Fac., Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (10), 1157–1160.—Generation of O from MnO_2, Co_3O_4, NiO and CuO, which are used to promote the oxidation of refractory organic nitrogen compounds, was examined at various temp. Pure Co_3O_4 starts to decompose at 750° and liberates O (6 ml at s.t.p. from 150 mg) at a const. rate between 800° and 950°. Since the O liberated at $> 800°$ is effective for the promotion of combustion, Co_3O_4 appears to be a satisfactory substitute for the conventional CuO powder.

XIII. Modification of apparatus for the Dumas nitrogen determination with a flow-checking device before the combustion tube and with cobaltic oxide as oxidising agent. Keiichiro Hozumi, Kazuo Imaeda and Shigeo Kinoshita. *Ibid.*, 1956, **76** (10), 1161–1166.—A new flow-checking device, making use of a glass capillary tube, is attached in front of the combustion tube in the Dumas micro-determination apparatus modified by Gysel. This

makes the gas flow uniform and also prevents the back-flow of the burnt gas. When Co_2O_3 is mixed with the sample, combustion is complete, provided that the fixed furnace is kept at 750° to 850°.

XIV. An improved method for burning the sample by the use of cobaltic oxide as a source of oxygen in the Dumas nitrogen determination. Keiichiro Hozumi and Shigeo Kinoshita. *Ibid.*, 1956, **76** (10), 1167–1169.—To facilitate complete combustion of refractory organic compounds, the sample is placed on a shallow platinum boat (width 3·5 mm, height 5·5 mm), and inserted into the tube. A nickel boat containing $\simeq$ 150 mg of Co_2O_3 is placed next to the platinum boat and the combustion is carried out at $>$ 850°. The residue can be examined after the combustion and weighed, when necessary. The results obtained for sulphathiazole, one of the most refractory compounds, were better than those obtained by the standard method. K. Saito

2994. **Determination of halides in organic compounds by the method of double combustion.** N. P. Volȳnskiĭ, G. D. Gal'pern and I. K. Chudakova (Inst. of Petroleum, Acad. Sci., USSR). *Zavod. Lab.*, 1957, **23** (1), 27–29.—The lamp method previously described (*Anal. Abstr.*, 1956, **3**, 764) is modified for the purpose of determining Cl, Br and I. G. S. Smith

2995. **Routine determination of nitrogen in the microgram range with sealed-tube digestion and direct nesslerisation.** F. L. Schaffer and J. C. Sprecher (Univ. Calif., Berkeley, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 437–438.—The sample is digested with H_2SO_4 in a sealed tube at 450° and the digest is tested with Nessler reagent. The extinction is then measured at 480 mμ. Recoveries in the range 1 to 16 μg of N were 100 $\pm$ 3%. The procedure was applied to the analysis of proteins. G. P. Cook

2996. **The micro-estimation of sulphur in organic compounds. Direct titration.** H. Wagner (Microanal. Lab. J. R. Geigy A.-G., Basle, Switzerland). *Mikrochim. Acta*, 1957, (1), 19–23. Sulphur is determined by direct titration, with $Ba(ClO_4)_2$, of the H_2SO_4 formed after combustion of the sample in O and absorption of the gases formed in H_2O_2. A mixture of thorin and methylene blue is used as indicator for the titration, which is carried out in 80% *iso*propyl alcohol. The combustion apparatus is described. Although Fritz and Yamamura (*Anal. Chem.*, 1955, **27**, 1461) state that many cations and anions interfere, it was found that, provided a platinum catalyst was not used, no interference due to phosphate, nitrate, chloride and fluoride was encountered on the micro scale. The analysis takes 15 to 20 min. and the accuracy corresponds to that of micro-analytical methods. P. S. Stross

2997. **Complexometry in organic analysis. V. Determination of carbon-carbon double bonds by means of mercuric acetate.** B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 259–263.—A soln. of mercuric acetate (**I**) reacts with C:C double bonds in the presence of $(C_2H_5)_2OBF_3$ (**II**) to give acetoxymercuri derivatives. The excess of Hg can be determined complexometrically. *Procedure*—Dissolve the sample (0·5 milli-equiv.) in a methanolic soln. of **II**, add **I** (150 mg exactly), mix until **I** is dissolved, set aside for 1 hr., or heat on a water bath under reflux. Add buffer soln. (54 g of NH_4NO_3 and 350 ml of 25% aq. NH_3 in 1 litre of water) (10 ml), 0·1 *M* EDTA (zinc salt) (10 ml), water (20 ml), and Eriochrome black T as indicator, and titrate with 0·05 *M* EDTA (disodium salt) till the colour turns blue. Make a blank determination. Twenty-four compounds were determined with the use of this procedure, with an error $\not> \pm$ 0·3%. The determination of linalol, oleic acid and 1:4-dihydronaphthalene must be carried out at room temperature to prevent side reactions. J. Zýka

2998. **Analysis for industry [determination of organic functional groups].** W. I. Stephen. *Ind. Chem. Mfr*, 1957, **33**, 34–36, 87–88.—Recent literature on the determination of alkoxyl and alkylimino groups, $\equiv C{\cdot}CH_3$ groups, active hydrogen, primary amino groups and ethylenes is reviewed. (43 references.) S.C.I. Abstr.

2999. **Ethylene analyser.** Z. Kapišinsky (Výskumný ústav acetylénovej chémie, Nováky, Czechoslovakia). *Chem. Průmysl*, 1957, **7** (2), 66–67.—The principle and construction of a new ethylene analyser based on the estimation of heat evolved in the chlorination of ethylene is described. The mixture to be analysed and the Cl are preheated and enter a reaction chamber filled with catalyst (cupric chloride on crushed brick). The chamber contains a thin platinum wire connected to a Wheatstone bridge circuit. In an example given, the flow of mixture analysed was 15 ml per min. and the flow of Cl 20 ml per min. Results in the table below give some idea of the performance of the instrument:

C_2H_4, %	5	10	20	31	44	55	65	80
mV	1·0	2·0	3·8	5·9	8·2	10·4	12·1	15·0

As Pt is affected by Cl at high temp., the wire was glass-coated. The catalyst was reactivated approx. every 1000 hr. by washing with trichloroethylene. A similar analyser can be constructed for other pairs of gases which react appreciably exothermally or endothermally in the liquid state, *e.g.*, H and O, CO and O, NO and O, C_2H_2 and HCl, H and Cl, H_2S and O. A. Grochowski

3000. **Determination of propylene derivatives present as impurities in ethylene oxide and its refining products.** V. S. Étlis and S. L. Belen'kaya. *Zavod. Lab.*, 1957, **23** (2), 163–165.—The oxides are transformed into chlorohydrins and then hydrolysed to glycols. Oxidation of the glycols with HIO_4 yields aldehydes which can be determined polarographically or colorimetrically. The sample (2·5 to 4 g) is mixed with 40 ml of 4 *N* HCl cooled in ice, the soln. is made up to 250 ml and 25 ml is transferred to an ampoule together with 4 g of $NaHCO_3$. The sealed ampoule is kept for 2 hr. at 100°, and the contents are then transferred to a 100-ml flask, neutralised with conc. HCl to a pH of 5 to 7 and diluted with water to 100 ml. An aliquot portion containing $\not>$ 0·05 g of the glycol is reacted in a current of N or CO_2 for 15 min. with 15 ml of 0·1 *M* HIO_4 [prepared by dissolving 10·7 g of $Na_3H_2IO_6$ in 200 ml of water and adding *N* H_2SO_4 (amount not stated) and water to 500 ml], after which 4 g of $NaHCO_3$ is added and the passage of gas is continued for 1·5 hr. at a rate of 120 to 150 ml per min. The formaldehyde is absorbed in 2% glycine soln. and the acetaldehyde from propylene oxide in 5% $NaHSO_3$ soln., which is treated with 0·1 *N* iodine to destroy the excess of $NaHSO_3$. Saturated $NaHCO_3$ soln. (10 ml) is then added and the soln. is titrated with 0·02 *N* iodine with the addition before

the end of the titration of 10 ml of a buffer soln. containing 4 g of borax and 5 g of Na_2CO_3 in 100 ml. Any aldehydes in the original sample must be allowed for. G. S. SMITH

3001. **Determination of acetylene in crude or distilled acetaldehyde.** O. Frehden and I. Brincoveanu. *Rev. Chim., Bucharest*, 1956, **7** (7), 433.—Most methods for determination of C_2H_2 are unsuitable since, in the presence of alkalis, acetaldehyde reduces $AgNO_3$ to Ag. The authors propose a modification of a method based on the liberation of HNO_3 from a neutral soln. of $AgNO_3$—

$$C_2H_2 + 3AgNO_3 \rightarrow (CAg \equiv CAg)AgNO_3 + 2HNO_3.$$

Excess of Ag is removed by NaCl and HNO_3 is estimated by titration. *Procedure*—Half fill a stoppered flask with 50% aq. acetone soln., add ice and 5 ml of $AgNO_3$ soln. (5%), and counterbalance or weigh. Add 10 to 20 g of the acetaldehyde to be tested and weigh again. The excess of $AgNO_3$ after the acetylene has reacted is pptd. with $\simeq$ 3 ml of satd. NaCl soln. The soln. is then titrated with 0·1 *N* NaOH. Both small and large admixtures of acetylene can be determined with a fair degree of precision. H. SHER

3002. **Separation and identification of organic peroxides with a chromato-strip.** Kazuhiro Maruyama (Fac. of Sci., Kyoto Univ., Sakyo-ku, Kyoto). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (10), 1496–1499.—A chromatographic strip was prepared on a glass plate (25 cm × 1·5 cm, or 25 cm × 3 cm), with a mixture of silica gel (80 mesh, 10 g) and starch (0·5 g) in $\simeq$ 30 ml of water and dried in a desiccator containing KOH. The sample soln. is spotted at a point 2 cm from one end of the strip and developed with a mixture of CCl_4 and acetone (2 + 1). Saturated KI soln. or a mixture of $Fe(NH_4)_2(SO_4)_2$ and KSCN is the best revealing agent. The R_F values of aliphatic acid peroxides and dialkyl peroxides are reproducible under given conditions of thickness and water content of the strip, the initial position of the spots and temp. Peroxides can be identified by comparing the R_F values with those of known peroxides under identical conditions. K. SAITO

3003. **Application of thermal diffusion to separation of aliphatic alcohols and fatty acids from their mixtures.** C. W. Blessin, C. B. Kretschmer and R. Wiebe (U.S. Dept. Agric., Peoria, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 408–409.—Very little or no separation occurs in binary mixtures of aliphatic alcohols and fatty acids. This failure is attributed to hydrogen bonding, which obscures structural differences. G. P. COOK

3004. **Oxidimetric determination of reducing sugar with sodium hypobromite.** Chozo Yoshimura and Mitsuo Kiboku (Fac. of Engng, Kinki Univ., Fuse, Osaka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (10), 1546–1548.—Sodium hypobromite (2 equiv.) quant. oxidises reducing sugar (1 equiv.) in > 2 *N* NaOH within 4 min. at room temp. When the mixture is heated to boiling-point, 1 equiv. of sugar reduces 6 equiv. of NaOBr within 2 min. Prolonged heating (up to 10 min.) brings about no difference in the stoicheiometric relation between them. The sample (5 to 125 mg of sugar) is made 6 *N* with NaOH soln. and treated with a known excess of NaOBr and KI; the product is made acid and titrated with $Na_2S_2O_3$. K. SAITO

3005. **Identification of organic compounds. XIV. Separation and identification of aliphatic aldehydes and ketones by paper chromatography.** J. Gasparič and M. Večeřa (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 287–291.—A rapid method for the separation and identification of aldehydes and ketones as their 2:4-dinitrophenylhydrazones, with the system dimethylformamide - *cyclo*hexane, is described. The relation between R_F values and the structure of the investigated compounds is discussed. The possibility of the separation of the *cis* and *trans* isomers of the 2:4-dinitrophenylhydrazone of furfuraldehyde is demonstrated. As little as 3 to 60 μg of 2:4-dinitrophenylhydrazones could be separated, and for the detection of the separated spots, a 1% ethanolic soln. of NaOH was used. J. ZÝKA

3006. **4-Substituted thiosemicarbazides as reagents for the characterisation of aldehydes and ketones. IV. 4-*p*-Chlorophenylthiosemicarbazide.** M. Perpar and M. Tišler (Inst. for Organ. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1957, **155** (3), 186–189.—4-*p*-Chlorophenylthiosemicarbazide is a suitable reagent for the characterisation of carbonyl compounds. It is used as described for 4-*p*-bromophenylthiosemicarbazide (*cf.* Tišler, *Anal. Abstr.*, 1956, **3**, 3079). J. H. WATON

3007. **Determination of acetone, butanol and ethanol in mixtures.** B. M. Nakhmanovich and N. A. Pryanishnikova (Dokshukinski Acetone Works). *Zavod. Lab.*, 1957, **23** (2), 165–167.—From the amounts of $K_2Cr_2O_7$ required for oxidising a mixture of acetone, butanol and ethanol at two different concn. of H_2SO_4, 30 to 35% and 67 to 69%, and an iodimetric determination of acetone, the contents of all three components can be determined. G. S. SMITH

3008. **Determination of traces of ketone in a carbinol by differential infra-red analysis.** W. H. Washburn and F. A. Scheske (Abbott Lab., North Chicago, Ill., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 346–347.—Determination of 0·1 to 1·0% of ketone has been achieved with an accuracy within ± 0·02% and a precision of ± 0·01% by using the difference method described. Unmatched cells are employed, differences in cell thickness being eliminated by running the unknown in the sample cell against the solvent plus major component in the reference cell and then reversing the positions of the solutions. As little as 0·03% of ketone can be detected, all determinations being carried out in the carbonyl stretching region. E. G. CUMMINS

3009. **The separation and determination of carboxylic acids from C_1 to C_6 by partition chromatography on a silica column. I. General study.** R. Raveux and J. Bové (Inst. Franc. de Rech. Fruitières Outre-Mer, 6 Rue de Général Clergerie, Paris, France). *Bull. Soc. Chim. France*, 1957, (3), 369–376.—The nature of the silica used in partition chromatography of organic acids, the methods by which absorption by the silica itself can be suppressed, and the nature and quantity of the aq. phase it can support are discussed. The length and width of the column of silica desirable for a separation are also discussed. The acids can be introduced on to the column in several ways, of which an aq. soln. as salts (subsequently hydrolysed by the acid in the aq. phase) has advantages for volatile

acids. The elution solvents used are discussed with particular reference to the possibility of esterification, and the methods of determining and identifying the acids in the eluate are discussed. There is a critical comparison of partition and ion-exchange chromatography for the separation of acids.

II. New proposed technique. J. Bové and R. Raveux. *Ibid.*, 1957, (3), 376–381.—Silicic acid (Mallinckrodt XNB-1) (8 g) without previous preparation is treated 1 ml at a time with 5 ml of 0·5 *N* H_2SO_4 to give a dry powder, which is transferred by means of $CHCl_3$ to the tube (40 cm × 12 mm). The acids to be chromatographed are dissolved in 0·5 ml of *N* H_2SO_4 and taken up by 1 g of the silica, which is transferred by rinsing with $CHCl_3$ to the top of the column and this is then covered with a disc of paper and some glass wool. The column is eluted with six different mixtures of *tert.*-butyl alcohol and $CHCl_3$ ranging in composition from 8:92 to 40:60. The elution with a total vol. of 660 ml occupies 14 hr. The efficiency of the separation is demonstrated with synthetic mixtures and vegetable extracts. The column can deal with 1·5 milliequiv., and butyric or propionic, acetic, fumaric, pyruvic, glutaric, succinic or lactic, α-oxoglutaric, *trans*-aconitic, oxalic or glycollic, malic, citric, *iso*citric and tartaric acids are separated and can be determined with an accuracy of ± 5%.

E. J. H. Birch

3010. **Determination of free sulphuric acid in the presence of water-soluble fatty acids.** N. K. Man'kovskaya and S. A. Udovenko. *Maslob.-Zhir. Prom.*, 1956, (3), 30–32; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,330.—In the presence of 90% acetone, the dissociation of fatty acids is so much reduced that these acids are not titrated with 0·5 *N* alkali. Sulphuric acid can therefore be titrated potentiometrically without interference by fatty acids.

C. D. Kopkin

3011. **Characterisation of long-chain fatty acids by infra-red spectroscopy.** R. A. Meiklejohn, R. J. Meyer, S. M. Aronovic, H. A. Schuette and V. W. Meloch (Dept. of Chem., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 329–334.—Infra-red spectra of pure synthetic solid fatty acids, C_{10} to C_{38}, are presented for the identification of unknowns by comparison. It is proposed that the region 7·4 to 8·5 μ in the potassium bromide disc spectra of straight-chain fatty acids and their sodium barium and silver soaps, the 'band-progression' region, be used to identify unknown fatty acids when comparison fails. The rule that 'the number of bands in progression series is equal to half the number of carbon atoms in the chain' in the 7·43 to 8·47-μ region, is proposed for straight-chain fatty acids with an even number of carbon atoms and extended to cover those with an odd number. The analysis of mixtures is discussed.

E. G. Cummins

3012. **The determination of alkali salts of organic acids by residual non-aqueous titration.** M. I. Blake (School of Pharmacy, North Dakota Agric. Coll., Fargo, N.D., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (3), 163–166.—The U.S.P. XV method of assay of the alkali-metal salts of organic acids is compared with a method in which back-titration in glacial acetic acid is used. The non-aqueous back-titration is rapid and accurate and is applicable to a variety of salts. It is particularly suitable for tartrates, which are poorly soluble in glacial acetic acid and are not readily determined by direct titration. *Procedure*—Dissolve the sample (1 milliequiv.) in a mixture of glacial acetic acid (30 ml) and 0·1 *N* $HClO_4$ in glacial acetic acid (25 ml) and back-titrate with 0·1 *N* Na acetate in glacial acetic acid, either potentiometrically or with methyl violet as indicator to a visual end-point (first permanent blue showing no trace of green).

A. R. Rogers

3013. **Determination of γ-butyrolactone and its derivatives. I. Colorimetric determination of γ-butyrolactone.** Satoshi Mizukami and Koichi Nagata (Res. Lab., Shionogi & Co. Ltd., Imafuku, Amagasaki, Osaka). *J. Pharm. Soc. Japan*, 1956, **76** (10), 1129–1133.—Formation of hydroxamic acid (**I**) from a lactone and hydroxylamine (**II**) was applied to the colorimetric determination of γ-butyrolactone. The rate of formation of **I** increases with pH and reaches a const. value at pH 11. The optimum pH for the colour reaction between **I** and Fe^{3+} is 0·7 to 1·3. Care must be taken to keep the pH constant for a stable coloration. Esters and acid amides interfere with the determination, but butanol and butane-1:4-diol do not. *Procedure*—Dissolve the sample (≃ 400 mg) in water (250 ml) and dilute a 10-ml portion to 100 ml. Heat the dil. sample soln. (5 ml) with basic **II** soln. (neutralise 25 ml of 3·0 *N* hydroxylamine hydrochloride with 3·0 *N* NaOH to a mixture of phenolphthalein and thymolphthalein, and make alkaline with 20 drops of the NaOH) (10 ml) at 40° for 20 min. Cool the product and mix with iron alum soln. (25 g of iron alum and 12·50 ml of 3·50 *N* HNO_3 in 250 ml) (10 ml), and measure the extinction at 505 mμ. K. Saito

3014. **Potentiometric determination of mercaptans in presence of elemental sulphur.** J. H. Karchmer (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 425–431.—In the potentiometric titration of thiols in petroleum with alcoholic $AgNO_3$, low results and poorly defined titration curves may be produced when the ratio of elementary S to thiol is > 1:1. This is attributed to the formation of inorganic polysulphides which interfere with the titration. The presence of air also produces deleterious effects. Improvement can be made by use of a more acidified solvent than that used normally (alcohol - benzene containing Na acetate) and by immediate titration of the sample under N. G. P. Cook

3015. **Use of iodine chloride in analytical chemistry. VII. Determination of thiosemicarbazide, bismuthon and dimercaprol.** J. Čihalík and J. Růžička (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 264–271.—*Procedure*—For thiosemicarbazide (**I**), dissolve 1 to 10 mg in a small vol. of ethanol, dilute to 100 ml with H_2O, and titrate potentiometrically with 0·1 *N* ICl. For bismuthon (5-mercapto-3-phenyl-2-thio-1:3:4-thiadiazolone) (**II**), dissolve 25 to 100 mg in H_2O, remove O and titrate with 0·1 *N* ICl. The corresponding disulphide is formed. For dimercaprol, dissolve 0·2 to 0·3 g in H_2O, remove O, make up to 50 ml, dilute 2 to 5 ml to 100 ml and saturate the soln. with Na acetate. Titrate with 0·1 *N* ICl. The error for **I** is ± 0·13%, and for **II** ± 0·4%. Silver and Cu can be pptd. with a soln. of **II** (Ag:**II** = 1:1, Cu:**II** = 1:2) and the excess of **II** can be determined with 0·1 *N* ICl without removing the ppt. J. Zýka

3016. **Sensitive photometric technique for determination of organophosphorus compounds.** F. T. Eggertsen and F. T. Weiss (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 453–455.—The method is based on the reduction of the phosphorus compound in a suitable solvent by addition of an ethereal soln. of lithium aluminium hydride. The PH_3 produced is passed through $AgNO_3$-treated indicator paper, with air as a sweeping gas, and the intensity of the spot formed is measured photometrically. Of several compounds tested, organo compounds were detected at the microgram level, whereas inorganic phosphorus material produced little response.

G. P. Cook

3017. **Analysis of organosilicon compounds. XVII. The qualitative analysis of technical alkoxy- and aroxy-silanes.** A. P. Kreshkov and V. T. Shemyatenkova. *Trudy Mosk. Khim. Tekhnol. Inst.*, 1954, (18), 67–72; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1276.—To detect aroxysilanes, use is made of the etherification reaction, proceeding according to the equation—

$(C_6H_5O)_4Si + 4C_2H_5OH \rightleftharpoons (C_2H_5O)_4Si + 4C_6H_5OH$.

Warm 5 to 40 mg of a phenoxysilane (**I**) with 1 or 2 ml of ethanol for 10 to 15 min. on a water bath; the esterification product of **I** gives reactions for phenol. The detectable minimum is 0·08 to 20 mg. Silicon tetrachloride in tetraethoxy- or tetramethoxy-silane is detected by the formation of I on warming with HI, starch or $Hg(NO_3)_2$ being used as indicator. With the latter, a red colour shows the presence of ethoxy- or methoxy-silanes, and a brown one, the presence of $SiCl_4$. Methoxy- and ethoxy-silanes in admixture with $SiCl_4$ may be detected by the reaction with borax; ethanol and methanol give a red colour with $Fe_4[Fe(CN)_6]$.

XVIII. The photocolorimetric determination of silicon in silicates derived from organosilicon compounds. A. P. Kreshkov and N. I. Gludina. *Ibid.*, 1954, (18), 73–76; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1276.—Dissolve the sample ($\equiv$0·00008 g of SiO_2 per ml) in 15 ml of 10% KOH soln. and dilute. Treat 5 to 15 ml of the soln. with 5 ml of a 5% soln. of $(NH_4)_2MoO_4$ in 10% acetic acid, add 5 ml of a saturated soln. of Na_2SO_3 and Na_2SO_4, warm for 5 min. and cool the resulting soln. of molybdenum blue. Treat with 20 ml of glycerol soln. (20 g per litre of ammonium oxalate, 20 g per litre of Na_2CO_3 and 150 ml per litre of glycerol), dilute to 100 ml, and after 1 hr. measure the extinction at 650 to 700 mμ.

C. D. Kopkin

3018. **Extrapolation plot for photometric titration of weak bases in aqueous and non-aqueous systems.** C. Rehm and Takeru Higuchi (Univ. of Wis., Madison, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 367–369.—The method is based on the use of relatively weak basic indicators, such that the changes in the indicator colour occur primarily after a basic sample has been titrated with an acid. The extrapolation of the stoicheiometric end-points from the absorbance - titration plots are from results well past the end-points. Data are given illustrating the application of the procedure to the titration of extremely weak bases in water and to the titration of practically non-basic compounds, such as urea and amides, in acetic acid. The accuracy is generally within $\simeq \pm$ 2%.

G. P. Cook

3019. **Micro-determination of primary amines. IV. Determination of aliphatic primary amines.** Daizo Shimoe (Kurosaki Facory, Mitsubishi Chem. Ind. Ltd., Kurosaki, Yawata). *Japan Analyst*, 1956, **5** (11), 617–620.—The modified Van Slyke method (*cf. Anal. Abstr.*, 1957, **4**, 2246) was applied to the analysis of aliphatic amines such as glycine and cystine. Since aliphatic amines react more slowly than aromatic with HNO_2, the amount of $NaNO_2$ must be increased (5%, 0·15 to 0·3 ml) to $\simeq$ 5 times the equiv. of the amine. The extent to which the "abnormal reaction" (*loc. cit.*) takes place is thus made negligible. Aromatic sulphonamide or guanidine compounds such as sulphanilamide or sulphaguanidine, which cannot be determined by the conventional Van Slyke method, can be determined by careful application of heat. Potassium bromide not only promotes diazotisation but also nitrosoation of an aromatic amine, resulting in "abnormal results." The addition of $CuCl_2$ (4 *M*, 1 to 2 ml) promotes the decomposition of the diazonium compound and, at the same time, suppresses the "abnormal reaction."

K. Saito

3020. **A modified Folin method for estimating primary and secondary amines.** K. Blau and W. Robson (King's College, Strand, London, W.C.2). *Chem. & Ind.*, 1957, (14), 424–425.—The method described was applied to chromatographic fractions. Folin's amino-acid reagent (1%) (0·5 ml) is added to the amine soln. (5 ml) containing $>$4 μmoles and B.D.H. universal buffer (pH 9·8) (2 ml). After 3 hr. in the dark, acetate buffer (pH 3) (0·5 ml) and $Na_2S_2O_3$ soln. (1 ml) are added to bleach the surplus reagent, and after 10 min. the extinction is read on a spectrophotometer at 476 mμ. The colour was inhibited or bleached by various metal ions, bleached by creatine and urea, and inhibited by dioxan or EDTA. Ammonia did not interfere.

D. P. Felix

3021. **Polarographic determination of benzene in the presence of its homologues.** V. Šedivec (Inst. Hyg. and Ind. Diseases, Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 249–253.—A new simple, rapid and accurate modification of the nitration method is described. *Procedure*—Dissolve the sample of benzene (5 to 100 mg) in glacial acetic acid (10 ml) and add a 0·5-ml aliquot to a nitration mixture (10 g of NH_4NO_3 in 100 ml of conc. H_2SO_4) (2 ml), mix and set aside for 5 to 10 min. Dilute with water (1 ml), add a satd. aq. soln. of CrO_3 (0·1 ml), and warm on the water bath (90° to 100°) for 30 min., adding more CrO_3 soln. on the appearance of a blue - green colour. Cool and add dropwise an aq. soln. of methanol until the blue - green colour reappears. Dilute with H_2O, add pyridine (10 ml), cool, add NaOH soln. (40%) (15 ml), mix and cool again. Shake with water, remove the lower green layer, wash the pyridine layer with NaOH (20%) (5 ml) and separate again. To the pyridine soln. add dil. nitration mixture (10 ml) and gelatin soln. (2 ml), make up to 50 ml with H_2O and register the polarographic wave. In this way benzene can be determined in the presence of its homologues. When determining benzene and the homologues together, add the soln. of the sample (0·5 ml) in glacial acetic acid to the nitration mixture (2 ml), dilute with H_2O, and add pyridine (10 ml). Cool, add gelatin soln., and adjust the vol. to 30 ml. Make a calibration curve (0·1 to 0·6 ml of the sample). The determination can be carried out in 1·5 to 2 hr.

J. Zýka

3022. **Infra-red absorption of the aldehydic C–H group. Ortho-substituted benzaldehydes.** S. Pinchas (Weizmann Inst. of Sci., Rehovoth, Israel). *Anal.*

Chem., 1957, **29** (3), 334–339.—Sixteen benzaldehydes, ten of which were substituted in the ortho position, have been measured in the aldehydic C–H region and the band positions tabulated. In all those in which the absorption had shifted from the region 2720 to 2745 cm^{-1} and 2812 to 2832 cm^{-1} to the region 2747 to 2765 cm^{-1} and 2860 to 2900 cm^{-1} it is suggested that the shift is due to bonding of the aldehydic C–H group. The band positions of ten benzaldehydes (3200 to 800 cm^{-1}) are listed and the origin of the 2820-cm^{-1} band is discussed. E. G. CUMMINS

3023. **The analysis of mixtures of benzenecarboxylic acids by partition chromatography.** B. Fishwick (Nat. Coal Board, Sheffield, England). *J. Chem. Soc.*, 1957, 1196–1199.—The components in a mixture of benzenecarboxylic acids can be separated, identified and quant. determined by partition chromatography, in a column (40 cm × 1·8 cm) of silica gel, with 0·5 *N* H_2SO_4 as stationary phase, *n*-butanol - $CHCl_3$ as mobile phase, and a flow rate of $\simeq$ 3 ml per min. The mixture of acids ($<$ 0·1 g) dissolved in methanol - $CHCl_3$ is added to the column followed by 50 ml of $CHCl_3$, and then (in successive 50-ml portions) 1050 ml of the mobile phase containing increasing concn. (2·5 to 70%) of *n*-butanol. The acid in each fraction of the eluate is titrated, after addition of 50 ml of H_2O, with 0·02 *N* NaOH, with phenolphthalein as indicator. Peak eluate vol. are given for several acids. Recoveries are generally $>$ 90%, and loss of acids through esterification can be avoided by substituting *tert.*-butyl alcohol or a ketone for *n*-butanol. W. J. BAKER

3024. **Polarographic determination of naphthalene as 1-nitronaphthalene.** V. D. Bezuglyĭ and N. D. Ogdanets. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 149–154; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,398.—Nitrate the naphthalene (0·0005 to 0·01 g) for 15 min. at 60° with 3 ml of HNO_3 (sp. gr. 1·33). An aliquot of the product is introduced into a soln. containing 0·2 *N* Na acetate in 50% methanol, hydrogen is passed and a polarogram obtained. In acid medium two waves are formed, with $E_{\frac{1}{2}}$ at 0·55 V and from − 1·0 to − 1·1 V with respect to an internal reference electrode. The second wave completely disappears in alkaline medium, but the height of the first remains constant in the pH range 2 to 13. The maxima in acid and alkaline media are suppressed by the addition of gelatin. With a naphthalene sample of 0·001 to 0·011 g, Ilkovic's equation is obeyed. When used for the determination of 0·000333 to 0·00062 g of naphthalene per litre in air, the error is $\gtrsim$ 3·6%. C. D. KOPKIN

3025. **Chromatographic separation of some anthraquinone derivatives.** L. Stárka and A. Vystrčil (Inst. Org. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 378–380.—A new method for the separation of aminoanthraquinones and hydroxy derivatives of anthraquinone and anthrone is described. Light petroleum containing 6% of $CHCl_3$ was used as mobile phase, and a mixture of ethanol and benzene (1:1) as solvent. The paper was impregnated with formamide. The separation of anthrone must be carried out in an atmosphere of SO_2 to prevent the reduction of anthraquinones. The separated spots can be observed in visible and u.v. light. The detection of anthraquinone was made by means of a methanolic soln. of Mg acetate (0·3%). The R_F values of 38 anthraquinones and 20 anthrones are given and the relation between R_F and substituents is discussed. J. ZÝKA

3026. **The detection of flavones and their decomposition products with stabilised diazonium salts by means of spot reactions.** R. Neu (Firma Dr. Willmar Schwabe G.m.b.H., Karlsruhe, Germany). *Mikrochim. Acta*, 1957, (2), 196–214.—Tests have been devised for the detection of microgram quantities of di- and tri-hydroxybenzenes and of aromatic hydroxy acids. The tests consist of spot reactions on filter-paper with stabilised diazonium salts to give characteristic dyes. Limits of detection and colours of the dyes in both daylight and u.v. have been studied with 28 flavones. D. F. PHILLIPS

3027. **Identification of organic compounds. XV. Identification of benzidine and its isomers.** M. Večeřa (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 292–301.—Derivatives of aromatic diamines, namely benzidine (**I**), diphenyline (**II**), *o*-benzidine (**III**), *o*-semidine (**IV**) and *p*-semidine (**V**), were prepared and a method for their micro-identification is proposed. Benzoyl derivatives were the most suitable for the identification of the diamines named. The identification can be confirmed by m.p., refractive index of molten deriv., and eutectic temp. X-ray diffraction data for the hydrochlorides of the diamines mentioned were also found to be suitable as means of identification. Bases of the diphenyl and diphenylamine type can be differentiated by means of the identification constants of their benzoyl derivatives, or by treating the bases with HNO_2 and recording the polarograms. The bases **I** to **V** can be differentiated in neutral or acid medium by means of their u.v. spectra, and isomers of **I**, **II** and **III** can be differentiated by their m.p., the eutectic temp. of their benzoyl derivatives, u.v. spectra, and the polarographic behaviour of their tetrazonium salts; **IV** and **V** can be differentiated polarographically. J. ZÝKA

3028. **Determination of pyrrole.** F. Fromm, R. Wilhelm and E. J. McGrady (Mount Mercy College, Pittsburgh, Pa.). *Proc. Pa Acad. Sci.*, 1956, **30**, 108–110.—A spectrophotometric procedure for the micro-determination of pyrrole is described. The sample is mixed in 0·5% acetic acid with 0·2 ml of 0·5% isatin soln. in glacial acetic acid and 1 ml of conc. HCl, and made up to 10 ml with 95% ethanol. The soln. is heated under reflux for 10 min., then cooled to room temp., and the vol. is readjusted to 10 ml with ethanol. The soln. is then measured in a Beckman (model B) spectrophotometer, with a blank mixture of the same proportions of isatin, conc. HCl and ethanol made up to 10 ml as compensation. The colour produced (pyrrole blue B) conforms to Beer's law over the range 0 to 40 mg of pyrrole per litre. The extinction is measured at 520 mμ, and a calibration graph is given. The reaction is specific for pyrroles with at least one free α-position. S.C.I. ABSTR.

3029. **Use of iodine chloride in analytical chemistry. VIII. Determination of some analytically important organic compounds.** J. Čihalík and K. Terebová (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 272–277.—A direct potentiometric determination of mercaptobenzothiazole (**I**), 8-hydroxyquinoline (**II**) and anthranilic acid (**III**) with ICl soln. is described. *Procedure*—Dilute 2 to 10 ml of 0·01 *M* **I** to between

50 and 100 ml, and titrate with 0·1 to 0·01 *M* ICl with starch as indicator, or potentiometrically. Dilute 0·5 to 2·0 ml of ethanolic 0·05 *M* **II** to 100 ml and titrate potentiometrically with 0·1 *M* ICl. This method is also suitable for micro-determinations; even 5×10^{-5} *M* soln. of **II** can be titrated. Soln. of **III** (2 to 5×10^{-4} *M*) can be titrated in slightly alkaline medium with 0·1 *M* ICl. The indirect determination of some metals can be carried out by pptg. them with an excess of the soln. of **I**, **II** or **III** and determining the reagent in the dissolved ppt., or the excess of reagent in the filtrate, by titration with ICl. The error for all the determinations was $\pm$ 0·5%. J. ZÝKA

3030. **Application of gas - liquid chromatography to analysis of liquid petroleum fractions.** D. H. Desty and B. H. F. Whyman (British Petroleum Co., Ltd., Sunbury-on-Thames, Middx.). *Anal. Chem.*, 1957, **29** (3), 320–329.—The gas density balance apparatus (*cf.* James and Martin, *Biochem. J.*, 1956, **63**, 144) has been used to determine the retention volumes of a large number of hydrocarbons and some sulphur compounds, boiling in the range from 30° to 150°. Benzyldiphenyl and *n*-hexatriacontane were used as stationary-phase liquids. An approximate molecular weight and a broad classification of an unknown as paraffinic, naphthenic, aromatic, etc., can be obtained from a plot of the logarithms of the relative retention volumes in the stationary-phase liquids against each other, since each homologous series produces a straight line approximately parallel to the others. The identification of small amounts of impurity in *iso*octane fuel samples was successful, in spite of necessary column overloading, to the extent of identifying methyl*cyclo*hexane, an unexpected impurity later confirmed. Hydrocarbons in individual peaks have been concentrated and examined in the mass spectrometer to confirm tentative identification. Results are tabulated and the unique potentialities of gas - liquid chromatography are emphasised. E. G. CUMMINS

3031 **Hydrocarbons in the 116° to 126° fraction of petroleum.** A. R. Glasgow, jun., R. J. Gordon, C. B. Willingham, B. J. Mair and F. D. Rossini (Carnegie Inst. Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 357–360.—Twenty-two hydrocarbons were found and this fraction constituted $\simeq$ 5·37% by vol. of the representative petroleum under investigation by A.P.I. Research Project 6. The compounds were concentrated by the usual distillation procedures and identification was made by spectrometric and other methods. The material is composed almost entirely of (*a*) normal paraffins (36% by vol.), (*b*) branched paraffins (30% by vol.), (*c*) alkyl*cyclo*pentanes (8%), (*d*) alkyl*cyclo*hexanes (26%) and *cyclo*heptane (0·15%). Concn. and other data of the individual compounds are listed. G. P. COOK

3032. **Esso lamp method for sulphur [in petroleum products].** C. C. Hale, E. R. Quiram, J. E. McDaniel, and R. F. Stringer (Esso Res. and Engng Co., Linden, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 383–388.—Several variations of the lamp method for determining S in petroleum products have been integrated into an apparatus and procedure for routine testing of $\simeq$ 20 samples daily. The sample (3 to 6 g) is burnt in a mixture of O and CO_2 and the products are absorbed in aq. 3% H_2O_2 soln. The S in the absorbent soln. is then determined (*i*) conductimetrically if the S content is > 0·1 mg, and the samples are free from Pb or acid-forming compounds other than S, (*ii*) nephelometrically (for Pb-free samples containing < 0·1 mg of S or leaded samples containing < 3 mg of S), or (*iii*) gravimetrically (for leaded samples containing > 3 mg of S). The nephelometric method is rapid for all samples with $\geq$ 0·06% of S, whilst the gravimetric method obviates the usual digestion and ignition. The standard deviation for (*i*) and (*iii*) is from $\pm$ 0·0008 to 0·015 for concn. of S of 0·01 to 1%, whilst that for (*ii*) ranges from $\pm$ 1·1 to 12 at concn. of S of 5 to 500 p.p.m. (12 analyses in each instance). In (*iii*), Naphthol yellow S is used to induce coarse pptn. of $BaSO_4$ (*cf. Anal. Abstr.*, 1954, **1**, 1183). W. J. BAKER

3033. **Determination of trace amounts of arsenic in petroleum distillates.** N. C. Maranowski, R. E. Snyder and R. O. Clark (Gulf Res. and Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 353–357.—The method is based on the wet oxidation of the sample, followed by isolation of the As on paper as the coloured reaction product of AsH_3 and $HgBr_2$. The intensity of the colour is measured quant. with a spectrophotometer fitted with a diffuse reflectance assembly. Recoveries of > 90% were obtained over the concn. range of 0·1 to 0·5 μg of As, and the standard deviation was $\simeq \pm$ 0·025 μg, calculated from 22 determinations of As added to petroleum samples. Antimony interferes in quantities > 100 μg. G. P. COOK

3034. **Purification, purity, and freezing-points of 20 A.P.I. standard and A.P.I. research hydrocarbons.** A. J. Streiff, L. H. Schultz, A. R. Hulme, J. A. Tucker, N. C. Krouskop and F. D. Rossini (Carnegie Inst. Technol., Pittsburgh., Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 361–363.—The hydrocarbons investigated included two paraffins, one cycloparaffin, nine mono-olefins, one diolefin, three cycloolefins, one dicycloparaffin, one cycloparaffin-aromatic, one cycloparaffin-olefin and one dinuclear aromatic. G. P. COOK

3035. **Determination of mono- and di-aromatics in mineral oil fractions.** H. Geelen, H. J. Waterman and J. B. Westerdijk (Univ. of Chemical Engng, Delft, Holland). *J. Inst. Petrol.*, 1957, **43**, 14–20.—Diagrams of sp. refraction, sp. volume and percentage of H, as functions of the reciprocal of the mol. wt. and of the mol. wt. of saturated oil fractions, are used to determine an "apparent ring number" of an aromatic fraction. A linear relation exists between this number and the average number of mono-aromatic rings, di-aromatic rings and naphthenic rings in the fractions. Equations are developed from which these ring numbers can be calculated from sp. refraction, sp. volume and mol. wt. The method is applicable to type concentrates prepared chromatographically. S.C.I. ABSTR.

3036. **Luminescence method of determining oils in industrial solutions of ammonium nitrate.** M. M. Korosteleva, S. I. Krichmar, E. A. Kopylova and A. K. Korotych (Dnieprodzerzhinsk Nitrate Fertiliser Works). *Zavod. Lab.*, 1957, **23** (1), 30.—To determine small amounts of oil (10^{-4} to 10^{-3} %) in soln. of NH_4NO_3 the sample (100 ml) in a separating funnel is extracted with 20 ml of CCl_4, the solvent layer is separated and evaporated to between 1 and 2 ml, the residue is transferred to a 5-ml flask, the soln. is diluted to the mark with CCl_4 and transferred to a cell for luminescence

analysis in the light of a mercury lamp, and the intensity is compared visually with standards.
G. S. SMITH

3037. **Determination of trace amounts of copper. Application of the bathocuproine [2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline] reagent to pulp, paper and pulping liquors.** L. G. Borchardt and J. P. Butler (Inst. Paper Chemistry, Appleton, Wis., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 414–419.—For the accurate colorimetric determination of 0·1 to 40 p.p.m. of Cu, the method in which the copper complex of 2:9-dimethyl-4:7-diphenyl-1:10-phenanthroline (Smith and Wilkins, *Brit. Abstr. C*, 1953, 288) is used is regarded as having greater sensitivity, specificity and simplicity than has either the dithiocarbamate method with EDTA, or the Zn dibenzyldithiocarbamate method. In the preferred procedure the organic matter in the sample (1 g or 10 ml) is first destroyed by digestion with HNO_3 (20 ml) and 72% $HClO_4$ (5 ml). The cool soln. (25 ml) is neutralised with conc. aq. NH_3 (Congo red indicator), adding 10 ml in excess, and is then transferred to a separatory funnel (100 ml) into which are added, in succession, 10% aq. hydroxylamine hydrochloride (2 ml), 0·01 *M* bathocuproine in *n*-hexanol (1 ml), and *n*-hexanol (5 ml). The soln. is shaken for $\simeq$ 2 min. and, after 5 min., the aq. layer is discarded and the extinction of the hexanol phase is measured at 479 mμ (1-cm cell, Beckman spectrophotometer) against that of a blank with all reagents. The blank should be extracted with bathocuproine in hexanol to remove residual Cu. Results obtained, by the three colorimetric methods, for samples of pulp, paper and liquor are reported.
W. J. BAKER

3038. **Systematic scheme of semi-micro qualitative analysis for anionic surface-active agents.** H. Holness and W. R. Stone (South-West Essex Tech. Coll., Walthamstow, London). *Analyst*, 1957, **82**, 166–176.—By the scheme described, an anionic surface-active agent can be assigned to one of 21 groups of commercially available products. An initial extraction with a light petroleum - ether mixture separates the active and inactive materials, and extraction of the aq. layer with *tert.*-butyl alcohol isolates the active material, which is then examined according to the scheme described. A mixture of two dyestuffs (Disulphine blue V200 and Dimidium bromide) of differing colour and charge in soln. at two pH values provides a reagent that differentiates the four main classes of active material when present as single substances, *viz*, fatty acid soaps, sulphated and sulphonated anionics, cation-active amines and quaternary salts. These indicator reagents also confirm the presence of cation-active and non-ionic surface-active agents present as single substances, but a qualitative scheme to include these has not yet been devised. The purpose and application of the identification tests are described.
A. O. JONES

3039. **Determination of the ionic form of surface-active materials by means of dye indicators.** R. Bennewitz (VEB Fettchemie, Karl-Marx-Stadt, Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (10), 832–833.—Above a certain critical concn., surface-active materials in soln. aggregate to form micelles that selectively adsorb one component of a dissociated acid - base indicator. An apparent pH change is thus produced; anionic materials shift all indicators to the acid side; cationic materials shift all indicators to the alkaline side; non-ionic materials shift indicator acids to the acid side and indicator bases to the alkaline side. Several indicators are examined to find those most suitable for determining the ionic form of surface-active materials. For the detection of anionic materials, alone or in the presence of non-ionic compounds, thymol blue (in 0·005 *N* HCl) is the most suitable; cresol red (in 0·1 *N* HCl) is the only other satisfactory indicator. For the detection of cationic materials, bromophenol blue (in standard acetate) is the most sensitive indicator; in doubtful cases thymol blue (in 0·1 *N* HCl) is also used. The non-ionic polyoxyethylene derivatives can only be distinguished clearly from cationic and anionic materials by the combined use of metanil yellow (in 0·1 *N* HCl) and bromophenol blue (in standard acetate), but non-ionic compounds cannot be detected when anionic or cationic materials are also present.
E. HAYES

3040. **Use of fluorescent indicators for the determination of small amounts of surface-active compounds. II. Determination of organic quaternary salts and bases.** M. Doležil and J. Bulandr (Výzk. ústav zušlecht'ování rud, Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 255–258.—The titration of cation-active quaternary salts, bases and amines can be carried out with the use of Na lauryl sulphate (**I**) as vol. reagent, and Na eosinate as indicator. *Procedure*—Dissolve the sample (0·25 g) in hot water and dilute to 250 ml. To an aliquot add Na eosinate soln. (0·2%) (0·05 ml), adjust the pH (3·5 to 9 for quaternary salts, 3·5 to 4·5 for amines), dilute to 50 ml and titrate with 0·01 *M* **I** in u.v. light, till the yellowish-green fluorescence reaches its max. An error $> \pm 1\%$ was obtained in the titration of cetyltrimethylammonium bromide, cetylquinolinium bromide and dodecyl aminoacetate.
J. ZÝKA

3041. **Physicochemical methods for estimation of esters and alcoholic constituents in essential oils. I. Quaternary mixture of two alcohols and two esters.** J. B. Lal, S. P. Srivastara and D. Prakash. *J. Proc. Oil Technol. Ass., India*, 1956, **12** (1), 68–76.—Four independent equations to evaluate the four variables (percentage of two alcohols and two esters) are derived. Two are based on the ester values of the mixture before and after acetylation. The third involves the additive nature of the sp. volume of the components. The fourth is based on the percentage composition of the mixture.

II. M. C. Joshi, J. B. Lal and A. K. Ghosh. *Ibid.*, 1956, **12** (1), 77–82.—The formulae derived were experimentally verified with 2-phenylethanol - cinnamyl alcohol, benzyl alcohol - anisyl alcohol, and 2-phenylethanol - anisyl alcohol.
S. C. I. ABSTR.

3042. **Estimation of alcoholic constituents and esters in essential oils. V. Mixture containing two alcohols and one ester.** M. C. Joshi, R. C. Srivastava and J. B. Lal (H. B. Technol. Inst., V.P. Kanpur). *J. Proc. Oil Technol. Ass., India*, 1956, **12** (1), 41–46.—The formulae proposed by Lal *et al.* (*Anal. Abstr.*, 1957, **4**, 2680) were experimentally verified with mixtures of terpineol, 2-phenylethanol and benzyl acetate, by using the formylation procedure.
S.C.I. ABSTR.

3043. **Chromatographic determination of the fractional composition of high polymers.** B. V. Losikov, N. I. Kaverina and A. A. Fedyantseva. *Khim. i Teknol. Topliva*, 1956, (3), 51–53; *Ref. Zhur.*,

Khim., 1957, Abstr. No. 1196.—Results are given of the chromatographic separation into fractions of poly*iso*butylene (**I**), with activated carbon and silica gel as adsorbent. Two samples of **I** were studied, of average mol. wt. 18,000 and 27,000. **I** was dissolved in *iso*octane in the proportion 1 to 10 or 1 to 12. For an approx. separation, a small column was used (length 1300 mm, diam. 17 mm); for more exact fractionation a larger column was used (length 1800 mm., diam. 26 mm). *iso*Octane and (in the later stages) benzene were used as eluents. Excellent agreement was obtained in the results of the chromatographic separation with those of the fractional pptn. of **I** from di*iso*butylene soln. by *n*-butanol. C. D. KOPKIN

3044. **Determination of ester groups of polyacrylic and polymethacrylic esters.** A. Ya. Drinberg, A. D. Yakovlev and Z. S. Sokolova (Lensovet Leningrad Tech. Inst.). *Zavod. Lab.*, 1957, **23** (1), 26.—The method is based on hydrolysis under pressure with 2 *N* KOH in ethanol - benzene soln. The sample of polymer (0·15 to 0·20 g) in a 40-ml ampoule, of length 190 mm, int. diam. 17 mm and wall thickness 2 to 3 mm, is dissolved in 3 ml of benzene and treated with 2·0 to 2·5 ml (accurately measured from a micro-burette) of a soln. of $\simeq$ 250 g of KOH in 1 litre of ethanol, with care that the soln. does not touch the neck of the ampoule. The liquids are shaken together and heated, if necessary, to give a clear soln. Complete clarity, however, cannot always be obtained. The ampoule is then sealed and, together with one or two blank ampoules similarly prepared but without the polymer, is placed in a thermostat at 120° (for acrylates to C_4), 140° (for higher alkyl acrylates), 160° (for methacrylates to C_4) or 180° (for higher alkyl methacrylates) for 3 to 4 hr. The reaction is complete when there is no further pptn. of the insol. potassium salt. The ampoule is then opened and the contents are gently heated with 4 to 5 ml of water to dissolve the ppt. The excess of KOH is titrated with 0·5 *N* HCl, with phenolphthalein as indicator.
G. S. SMITH

3045. **Simplified method for analysis of alkyd resins.** A. Davidsohn. *Peint-Pigm.-Vern.*, 1957, **33** (3), 230.—The alkyd resin is saponified with ethanolic KOH (0·5 *N*) and diluted with H_2O to give a 50% ethanolic soln., which is acidified with HCl to methyl red indicator. The fatty (and any rosin) acids are then extracted with light petroleum and weighed, and their acid values are determined. The phthalic anhydride content (in the absence of other dibasic acids) is calculated from the sap. value of the resin and the content and acid value of the fatty acids. If oxidised or castor oil fatty acids are present, the fatty acids are extracted with ether instead of light petroleum and the extract washed with H_2O. L. A. O'NEILL

3046. **Methods of testing plastics I. Effect of temperature.** British Standards Inst. B.S. 2782: Part 1: 1956, 62 pp.—Methods are recommended for measuring crushing strength after heating, deformation at elevated temp., melting-point, mechanical properties at low temp., flow properties, shrinkage and after-shrinkage, and loss in weight on heating. G. S. ROBERTS

See also Abstracts 2875, 2876, 2877, 2878, 2880, 2899, 2917, 3135, 3136, 3161, 3181, 3190.

4.—BIOCHEMISTRY

INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

3047. **A simple electrometric technique for the determination of carbon dioxide tension in blood and plasma, total content of carbon dioxide in plasma, and bicarbonate content in "separated" plasma at a fixed carbon dioxide tension (40 mm Hg).** P. Astrup (Centr. Lab., Rigshospitalet, Copenhagen). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 33–43.—The apparatus is a modification of the one described earlier (*Anal. Abstr.*, 1957, **4**, 3174). The water-jacketed chamber which houses the electrode has two additional connections leading to a second water-jacketed chamber which is used for moistening the gas mixtures. These gas mixtures can be admitted to the electrode chamber where they are mixed with the blood by a plunger-agitator operated by a pulsator moving at 3 c/s. The technique is based on the relation between pH and pCO_2. Determination of pCO_2 and the bicarbonate content of separated plasma at pCO_2 of 40 mm Hg was found to be possible with an accuracy better than $\pm$ 3%. The effect of varying protein concn. on pH and pCO_2 at 38° are shown. A comparison is made with manometric methods. E. KAWERAU

3048. **Spectrophotometric determination of haemoglobin oxygen saturation in haemolysed whole blood.** H. E. Refsum and S. L. Sveinsson (Centr. Lab., Ullevål Hospital, Oslo). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 67–70.—The optical density of oxyhaemoglobin is measured at both the maximum (576 mμ) and the minimum absorption (560 mμ) of oxyhaemoglobin with a spectrophotometer, the oxygen saturation being calculated from the formula of Drabkin. Parallel determinations with the manometric method were carried out on the same samples of blood and good agreement was found between the two methods. Advantages of the spectrophotometric method and sources of error of the procedure are discussed. E. KAWERAU

3049. **The collection of urine for ammonia determination.** L. Goldstein, R. Richterich-van Baerle and E. H. Dearbern (Boston Univ. Med. Sch., Mass., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (2), 324–328.—Bacterial growth in the collection of 24-hr. urine samples from laboratory animals is eliminated by adding 20 ml of *N* HCl to the collecting jar. The sample is then titrated electrometrically to pH 7·4 for NH_3 determination.
W. H. C. SHAW

3050. **Semi-quantitative method for determination of lithium in small amounts [in serum].** C. M. Plum ("Filadelfia" Hosp., Dianalund, Denmark). *Clin. Chim. Acta*, 1957, **2** (1), 67–69 (in English).—Add 1·0 ml of trichloroacetic acid (10%) to 1·0 ml of unhaemolysed serum, mix, allow to stand for 10 min. and centrifuge for 10 min. at high speed. Mix 0·9 ml of supernatant liquid with 0·1 ml of 2 *N* KOH, add 1 ml of saturated aq. NaCl soln. and then 2·0 ml of periodate reagent (dissolve 2·00 g of KIO_4 in 10 ml of 2 *N* KOH, add 50 ml of H_2O then 3 ml of 10% $FeCl_3$ soln. and dilute to 100 ml with freshly prepared 2 *N* KOH; the soln. keeps for a week when stored in a refrigerator). Place in a water bath at 50° for 1 min., cool at room temp. for 5 min., and read against H_2O at 720 mμ.

Prepare a blank with H_2O instead of serum and a standard curve by adding Li_2CO_3 to normal pooled serum in concn. of 0·5 to 2·0 milli-equiv. per litre. The results are not sufficiently reproducible for exact determinations but give an approx. value for clinical use. H. F. W. KIRKPATRICK

3051. **Calcium analysis in patients being treated with EDTA.** M. H. Carr and H. A. Frank (Veterans Admin. Hosp., Kansas City, Mo., U.S.A.). *Clin. Chem.*, 1957, **3** (1), 20–21.—The sample may be ashed before analysis, but a simpler method which gives comparable results is to acidify the soln., after addition of oxalate, by adding acetic acid to a pH of 3·0 to 5·0, with bromocresol green as indicator, when Ca is pptd. quantitatively.
H. F. W. KIRKPATRICK

3052. **Determination of mercury in urine.** V. L. Miller and F. Swanberg, jun. (State Coll. of Washington, Puyallup, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 391–393.—The procedure, which is rapid and specific for the diagnosis of chronic mercury poisoning, permits the micro-determination of 1 to 8 μg of Hg per 100 ml of urine or very dil. soln. of Hg. The sample ($\geq$ 100 ml) is oxidised catalytically with 50% H_2O_2 at 100° and the Hg^{2+} in the soln. (filtered if Bi or Ag is present) are converted into $2RHg^+$ (R = diaryl) with di-*p*-tolylmercury at pH 3 to 3·5 (Polley and Miller, *Anal. Abstr.*, 1955, **2**, 3420). The RHg^+ are then determined by extraction into $CHCl_3$, followed by treatment of the extract with an excess of dil. dithizone soln. in the presence of 0·3 *N* acetic acid. The extinction of the excess of dithizone is then measured in a Beckman spectrophotometer at 620 mμ, and the concn. of Hg is calculated from the working curve (0 to 8 μg of Hg plus all reagents). The catalytic mixture [6 *N* HCl containing 1 g of $FeCl_3.6H_2O$ and 2 g of $K_2SO_4.Cr_2(SO_4)_3$ per 100 ml] accelerates the rate of digestion of the sample and improves the percentage recovery of the Hg. The max. deviation is $\pm$0·80 μg (ten analyses). The method of Polley and Miller is slightly modified to shorten the procedure. W. J. BAKER

3053. **Simple improved method for the determination of serum iron.** T. Peters, T. J. Giovanniello, L. Apt and J. F. Ross (Veterans Admin. Hosp., Boston, Mass., U.S.A.) *J. Lab. Clin. Med.*, 1956, **48** (2), 280–288.—The serum sample (2 ml) is treated with 0·2 *N* HCl (3 ml) and thioglycollic acid soln. is added (one drop). After 30 min., 30% aq. trichloroacetic acid (1 ml) is added, and after being mixed, covered with a paraffin film and set aside for 30 min., the soln. is centrifuged. The supernatant liquid (4 ml) is treated with satd. aq. Na acetate (0·5 ml) and 2·0 ml of bathophenanthroline soln. [0·02% of reagent (4:7-diphenyl-1:10-phenanthroline) in *iso*propyl alcohol - *iso*amyl alcohol, 3:1]. The colour is measured at 535 mμ or with a green filter after 15 min. and compared with Fe standards. The method gives quant. recovery and is applicable to normal and abnormal serum and plasma samples. W. H. C. SHAW

3054. **Determination of total urinary oxalate.** C. L. Yarbro and R. E. Simpson (N. Carolina Univ., Chapel Hill, N.C., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (2), 304–310.—In a modification of the ether-extraction method of Powers and Levatin (*J. Biol. Chem.*, 1944, **154**, 207) the extraction period is increased to 18 hr. and the use of peroxide-free ether is recommended. Pptn. of the oxalate with aq. $CaCl_2$ is carried out at pH 4·0 to 4·5, at which value pptn. of calcium phosphates is avoided. Quant. estimation of total oxalate (oxalate plus oxaluric acid) is attained. The normal daily adult excretion is 20 to 40 mg. W. H. C. SHAW

3055. **The mercuric chloride turbidity test.** N. F. Maclagan, A. Bendandi and K. B. Cooke (Westminster Hosp. Med. School, London, England). *Clin. Chim. Acta*, 1957, **2** (1), 49–60.—The Takata - Ara reaction is presented in a simpler and more standardised form. Two techniques that give identical results are described. (*i*) Mix 0·2 ml of serum in a test-tube (4 in. $\times$ 0·5 in.) with 4 ml of phosphate buffer [(0·4 *M*, pH 12·3) 2 vol. of 0·4 *M* Na_2HPO_4 with 1 vol. of 0·4 *M* NaOH] and 0·6 ml of 0·5% $HgCl_2$ soln. (*ii*) Mix 0·1 ml of serum in a similar tube with 2·5 ml of phosphate buffer and 0·5 ml of 0·4% $HgCl_2$ soln. Then set the resulting mixture from (*i*) or (*ii*) aside for 30 min. and read the turbidity against protein standards, either visually or photometrically. One unit is defined as the turbidity produced by 1 ml of a dil. serum containing 10 mg-% of protein with 3 ml of 3% sulphosalicylic acid. The normal range is 0 to 4 units. The test appears to be of most value in the diagnosis of hepatic cirrhosis.
H. F. W. KIRKPATRICK

3056. **Identification and quantitative determination of keto acids by paper chromatography.** E. Kun and M. Garcia-Hernandez (Wisconsin Univ., Madison, U.S.A.). *Biochim. Biophys. Acta*, 1957, **23** (1), 181–186.—The method is suitable for use with biological materials and is based on the formation of the 2:4-dinitrophenylhydrazine derivatives (**I**). Preliminary separation from the derivatives of other carbonyl compounds is carried out, when necessary, by descending chromatography on Whatman No. 1 paper with light petroleum - 95% ethanol (1:4) for 4 to 6 hr. at 20°. The bis-**I** of glyoxal and methylglyoxal remain at the point of application and the **I** of non-acidic carbonyl compounds move as a group below the keto-acid derivatives. Each group is cut from the paper and eluted with ethyl acetate for quant. determination or re-chromatography. The extracted keto acid **I** are chromatographed on Whatman No. 1 paper impregnated with 0·1 *M* phosphate buffer (pH 7·3) and dried. After application of 1 μmole of **I** and equilibration with 95% ethanol, descending development is carried out with absolute ethanol - water (83:17) for 14 to 18 hr. at 20°. Each component is eluted separately and mono-**I** determined from the extinction at 365 to 370 mμ in phosphate buffer. The method is quant. and the accuracy is within $\pm$ 20%. Bis-**I** are determined in *N* NaOH at 560 mμ. Identification is by comparison with, and re-chromatography after admixture with, known compounds, and also by catalytic reduction to the corresponding amino acid with H and Pt. The amino acids are then studied chromatographically with conventional solvent systems.
W. H. C. SHAW

3057. **Spectrophotometric determination of the bile acids of serum.** P. Metais, H. Deiss and J. Warter (Clin. Méd. A, Fac. Méd., Strasbourg). *Bull. Soc. Chim. Biol.*, 1957, **39** (2–3), 321–329.—The blood, collected without anticoagulant, is centrifuged and 0·5 ml of serum is added to 10 ml of absolute ethanol, and heated at 80° for 5 min. and the ethanol layer is transferred to a flask. After two further washings with ethanol at 80°, the

combined extracts are evaporated slowly at 80° to 85° and the cooled residue is freed from lipids by careful washing with anhydrous ether. The washed residue is treated with 4 ml of H_2SO_4 (65%, v/v), shaken, and allowed to stand for 1 hr., after which the optical density of the soln. is read at 312·5 mμ. After correction for the basal optical density of the serum, the result, multiplied by 521, gives the deoxycholic acid (mg) per litre of serum. The basal density of the serum is calculated from readings taken at 250, 345, 375 and 410 mμ, and three equations are given, the one to be used being selected according to the character of the serum under examination. The error rarely exceeds 3%. Results and absorption curves are given for cholic, deoxycholic, glycocholic and taurocholic acids, from which it appears that the two former give peaks at 312·5 and 380 mμ, the two latter, and also glycodeoxycholic acid, one peak at 312·5 mμ.

R. E. Essery

3058. **Separation of coproporphyrins I and III by paper chromatography.** V. Holeček (Inst. Hyg. and Ind. Diseases, Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 315–318.—A new method for the separation of coproporphyrins I and III in the mixture lutidine - water has been developed, and the method for the separation of the methyl esters of both isomers in the mixture light petroleum - propanol (20:3) has been revised. For the detection of the separated compounds, u.v. light is suitable.

J. Zýka

3059. **Determination of urinary uroporphyrin by a direct extraction method.** E. I. B. Dresel, C. Rimington and B. E. Tooth (Univ. Coll. Hosp. Med. School, London). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 73–78.—The method is suitable for the investigation of suspected cases of porphyria and porphyrinuria and has advantages over other methods as it measures both coproporphyrin and uroporphyrin (I and III), the latter directly and not by difference. *Procedure*—Coproporphyrin is removed from the urine (50 ml) by shaking twice with glacial acetic acid (10 ml) and ether (100 ml). Uroporphyrin carried over into the ether is recovered by washing the ether with satd. Na acetate soln. (30 ml) and returning the latter to the urine. The urine is then adjusted to pH 1·5 with conc. HCl and extracted twice with *cyclo*hexanone (50 ml). Light petroleum (boiling range 40° to 60°) (100 ml) is then added to the *cyclo*hexanone and the mixture is repeatedly extracted with small amounts of 2% HCl until all uroporphyrin has been removed, as shown by fluorescence. For quant. determination, readings are taken in the spectrophotometer at 404 to 405 mμ and also at 380 mμ and 420 mμ and the correction formula of Rimington and Sveinsson is applied. $E^{1\%}_{1cm}$ for uroporphyrin is taken as 6517. Some of the steps in the extraction procedure have to be repeated when the porphyrin content is very high, and a slightly modified procedure in the final extraction is necessary when the content is very low as in normal urine. Recoveries at the 20 μg per litre level were 66 to 68%, at the 100 μg per litre level 73 to 89% and at the 1 mg per litre level 90 to 100%.

E. Kawerau

3060. **Ultra-micro method for [determination of] serum bilirubin by diazo blue reaction.** R. E. Stoner and H. F. Weisberg (Mt. Sinai Hosp., Chicago, Ill., U.S.A.). *Clin. Chem.*, 1957, **3** (1), 22–36.—To 0·2 ml of diazo reagent (Van den Bergh) add 0·02 to 0·05 ml of serum; if colour develops, allow 10 min. for completion, otherwise proceed immediately. Add 0·1 ml of conc. HCl and 0·2 ml of saturated $(NH_4)_2SO_4$, with mixing. Prepare a blank omitting the serum, dilute both soln. to 2·0 ml with absolute ethanol, stopper the tube and shake vigorously for 1 min. and leave lying horizontally for 10 min. Centrifuge at 2000 r.p.m. for 5 min., remove the supernatant liquid and read the colour at 580 mμ. Prepare a standard curve by adding 0 to 0·2-ml aliquots of a soln. of bilirubin (**I**) in $CHCl_3$ (0·04 mg per ml) to 1 ml of absolute ethanol, add with mixing 0·2 ml of diazo reagent, 0·1 ml of conc. HCl and absolute ethanol to 2·0 ml. After 15 min. read at 580 mμ. This method measures total **I**; a method for measuring 1-min. **I** is also given.

H. F. W. Kirkpatrick

3061. **Spectrophotofluorimetric studies of 5-hydroxyindoles and related compounds.** H. Sprince, G. R. Rowley and D. Jameson (Veterans Admin. Hosp., Coatesville, Pa., U.S.A.). *Science*, 1957, **125**, 442–443.—Data are presented for activation and fluorescence maxima, the widest range in which these maxima are suitable for concn. measurements, and the range of concn. within this range that shows linear fluorescence response. The instrument used is the Aminco - Bowman scanning spectrophotofluorimeter.

H. F. W. Kirkpatrick

3062. **Determination of linoleic, linolenic and arachidonic acids in milk and in blood. III. Determination in blood.** F. Corsini (Ist. di Clin. Ped., Univ. Bologna, Italy). *Acta Vitamin., Milan*, 1956, **10**, 64–69.—A spectrophotometric method is given for the estimation of the three acids on the same sample. *Procedure*—The sample of blood serum (2 ml) is added to 50 ml of Bloor's reagent (3 parts of abs. ethanol to 1 part of diethyl ether), and the soln. is refluxed on the water bath for 15 min. After filtration, and washing with 10 ml of reagent, 2 ml of 10% KOH soln. is added and the soln. is again refluxed for 15 min. Immediately afterwards, the ethanol and ether are evaporated off by warming under vacuum. To the residue are added 2 ml of H_2O and 4 ml of 12% H_2SO_4, and then two extractions are made with 50-ml portions of ether. The combined extracts are washed with 100 ml of H_2O, dried with 10 g of anhyd. Na_2SO_4, and concentrated in a 50-ml standard flask. For the isomerisation, 10-ml portions are evaporated in alkali-resistant test-tubes, and 0·35 ml of KOH in ethanediol is carefully added. The tubes are immersed for 30 min. in a phosphoric acid bath at 180°. The soln. are made up to 25 ml with absolute ethanol, and a blank is prepared from the reagent. Extinction measurements are made at 234, 268 and 316 mμ, that at 234 mμ after four- or five-fold dilution. Another 10-ml aliquot, after evaporation, is dissolved in absolute ethanol and its extinction (as well as that of the blank) is deducted from that of each of the other three aliquots. The amounts of the three acids are calculated from the absorption coeff. given by Beadle and Kraybill (*J. Amer. Chem. Soc.*, 1944, **66**, 1932). The results show good reproducibility, but owing partly to the small amount of linolenic acid in blood, and partly to the presence of acids with more than four double bonds, values for linolenic acid in human blood are frequently negative.

J. H. Waton

3063. **The official method for the determination of ethanol in blood.** L. Truffert. *Ann. Falsif.*, 1957, **50**, 59–64.—Details of procedure, the prescribed apparatus and the mode of expression of results, as

laid down in the official French method, are criticised. It is suggested that a limit of the order of 1 g of ethanol per kg of blood be accepted as the concn. above which legal proceedings can be instigated without risk of miscarriage of justice.

G. H. FOXLEY

3064. **Determination of *p*-aminobenzoic acid in urine.** L. A. Mokhov and Yu. F. Udalov. *Lab. Delo*, 1956, **2** (4), 19–20.—The sample (25 ml) of urine made just acid to Congo red with 2 *N* HCl is boiled under reflux for 15 min. to hydrolyse acetylated *p*-aminobenzoic acid, and then shaken vigorously for 15 min. with 0·5 g of activated wood charcoal (prepared by boiling 50 g of charcoal in 250 ml of 5% Na_2CO_3 soln. for 20 min., filtering, washing with hot water, treating with steam for 1 hr. and drying at 100° to 120°). The charcoal is filtered off, washed first with hot water and then with a mixture (1:1) of ether and ethanol so that the urine pigments are completely removed, and finally dried at $> 100°$. A suitable amount of the charcoal, *e.g.*, 100 mg, is boiled under reflux for 1 or 2 min. with 9 ml of water and 1 ml of satd. Na_2CO_3 soln. After filtration, 2 ml of the cooled soln. is stirred with 1 ml of 2 *N* HCl and 0·5 ml of 2% $NaNO_2$ soln. and set aside for 10 min. Cryst. Na acetate (200 mg) is dissolved in the diazotised soln., which is then tested with Congo-red paper. If the paper turns blue, additional Na acetate is added. One drop of 0·5% 1-amino-8-naphthol-3:6-disulphonic acid soln. is mixed with 2·5 ml of satd. Na_2CO_3 soln., which is then vigorously stirred with the diazo soln. and set aside at room temp. for 15 min. The colour is compared with that of a scale of standards, or the extinction is determined photometrically. Sulphonamides interfere.

G. S. SMITH

3065. **Quantitative determination of barbital [barbitone] in blood serum by ultra-violet absorption spectrophotometry.** R. Askevold and F. Løken (Centr. Lab., Ullevål Hospital, Oslo, Norway). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 1–5.—Barbiturates are quant. determined by their u.v. absorption at 239 mμ in a borate buffer at pH 10 and in acid solution. The novelty of the procedure consists in the treatment of the serum, which is extracted as follows: $CHCl_3$ (15 ml) is pipetted into a dry stoppered test-tube and to this are added in order anhyd. Na_2SO_4 (2 g), conc. HCl (0·1 ml) and serum (3 ml). After shaking vigorously, another 2 g of anhyd. Na_2SO_4 is added and shaking is repeated. More Na_2SO_4 is added if, after separation, the $CHCl_3$ layer is not free from droplets of water. A blank omitting the serum is also prepared. The soln. are then filtered, 5 ml of filtrate is extracted with an equal vol. of borate buffer (pH 10) and read in the spectrophotometer against the blank. The reading is repeated after rendering the solution acid by the addition of 0·05 ml of conc. HCl and stirring, and the amount of barbiturate is calculated from the difference of the extinction values. Recoveries vary from 80 to 110% (mean 96%). The interference of sulphonamides and salicylates is discussed.

E. KAWERAU

3066. **A new detection method in paper chromatography of sugars.** A. Heyrovský (Charles' Univ., Prague, Czechoslovakia). *Biochim. Biophys. Acta*, 1956, **21** (1), 180.—Two reagents based on indol-3-ylacetic acid for the detection of ketoses and ketose-containing saccharides on paper chromatograms are described.

W. H. C. SHAW

3067. **A method of estimation of 2-deoxyribose.** V. S. Waravdekar and L. D. Saslaw (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Biochim. Biophys. Acta*, 1957, **24** (2), 439.—The method described is based on the oxidation of 2-deoxyribose with HIO_4, and subsequent colorimetric estimation of the malonaldehyde formed, by treatment with 2-thiobarbituric acid. A 0·2 to 12·5-μg sample is required, and the method may also be applied to deoxyadenosine and deoxyribonucleic acid after hydrolysis.

W. H. C. SHAW

3068. **Use of thymol - sulphuric acid reaction for determination of carbohydrates in biological material.** M. R. Shetlar and Y. F. Masters (Univ. Okla., Oklahoma City, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 402–405.—Different absorption spectra are given by nearly all sugars when they are made to react with thymol in the presence of H_2SO_4. The Beer - Lambert law is obeyed reasonably well in the 10 to 100-μg range and glycosidic linkages do not affect the reaction. The presence of protein has a slight effect on the absorption spectra, but this appears to be due to reaction of the protein with H_2SO_4 and does not involve the thymol. The method was applied to the determination of the carbohydrate bound to protein, in 22 samples of human serum, and the results were in close agreement with those obtained by an accepted procedure. Absorption data for 17 sugars are listed.

G. P. COOK

3069. **A new micro-method for the estimation of [bacterial] cellulose.** G. G. Dearing (Nat. Res. Lab., Ottawa, Canada). *Nature*, 1957, **179**, 579.—In the procedure, which is based on that described by Mendel *et al.* (*cf. Anal. Abstr.*, 1954, **1**, 1590), the sample of bacterial cellulose is pretreated with 4% (w/v) NaOH soln., washed and centrifuged (with the addition of talc). The weighed, air-dried sample is then suspended in a vol. of H_2O such that the concn. of cellulose is < 150 μg per ml. Three times this vol. of H_2SO_4 (96%, w/v) is added dropwise with shaking, the test-tube is then heated for exactly 6·5 min. at 100° (water bath) and cooled. The pink soln. is centrifuged and its extinction is measured spectrophotometrically at 520 mμ. The concn. of cellulose is obtained from the linear standard curve for glucose (0 to 150 μg per ml). Cellulose recovery is $> 90\%$, and an analysis can be made in approx. one-half of the time required for the Schramm and Hestrin micro-method (*Biochem. J.*, 1954, **56**, 163).

W. J. BAKER

3070. **Separation of amino acids on columns of anion-exchange resins.** P. N. Campbell (Courtauld Inst. Biochem., Middlesex Hosp., London). *Biochim. Biophys. Acta*, 1956, **21** (1), 167.—From an investigation into the influence of the percentage of cross-linking agent in De-Acidite FF, it is concluded that the optimum is slightly less than 6%.

W. H. C. SHAW

3071. **Microdesalter for qualitative paper chromatography of amino acids.** G. Zweig and S. L. Hood (C. F. Kettering Foundation, Yellow Springs, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 438–441.—The principle of the microdesalter is that desalting is carried out directly on the chromatographic filter-paper, which is then developed by suitable paper-chromatographic techniques. The procedure permits the rapid desalting (1 to 5 min.) of small vol. of soln. (5 to 25 μl). The actual desalting is carried out by electrolysis as in the original

technique (*cf.* Consden *et al.*, *Brit. Abstr. C*, 1948, 61). Application of the instrument to the determination of amino acids in biological samples gave improved resolution of the ninhydrin-developed amino-acid spots. G. P. Cook

3072. **Separation of amino acids by paper electrophoresis. Studies on the migration distance of amino acids.** Kiyoshi Sakamoto and Kazuko Takeoka (Junior College, Kagoshima Prefectural Univ., Yamashita-cho, Kagoshima). *J. Agric. Chem. Soc. Japan*, 1956, **30** (8), 463–469.—The paper electrophoresis of various amino acids was studied at various pH values near the iso-electric point, and a new method of expressing the mobility is proposed. Each amino acid migrates, under given conditions of the composition of the soln., potential and current, towards a definite point, at a rate that decreases with time. This point is shifted towards the anode with increase in current. The rate of migration does not increase linearly with potential, but the mutual distance between spots of any two amino acids is proportional to the applied potential. When the distance of the spots of asparagine and glycine is taken for the standard, its ratio to that between the spots of glycine and a given amino acid remains constant, irrespective of the potential, current, time for electrolysis, length of the paper and the position of the initial spot. K. Saito

3073. **Modification of the method of zonal electrophoresis for preparative purposes.** Yu. A. Khavkin (Biochemistry Branch of the V. M. Molotov Tashkent Med. Inst.). *Lab. Delo*, 1957, **3** (1), 11–14.—One end of a strip of filter-paper (27 to 30 cm) is immersed in a buffer soln. (borate or barbitone) (pH 8·6). When the liquid has reached the middle of the strip the other end is immersed and when there remains only 3 to 3·5 cm of dry paper the sample of serum is applied in this region as a line 1·5 to 2 cm wide. The middle of the strip is held below the ends so that the buffer soln. restricts the applied serum to a band 0·7 to 1 cm wide at a distance of 8 to 10 cm from the cathode end. The strip is placed on a waxed glass plate or, preferably, a hammock of waxed threads, and buffer soln. is applied at the ends by means of pieces of filter-paper. A current (4 to 5 mA per 1-cm width and 80 V) is passed for 24 hr. The paper is then treated with a 0·5% soln. of bromophenol blue in methanol saturated with $ZnCl_2$. The method permits the preparation of material for the chromatographic determination of amino acids, the study of labelled compounds in proteins, and the study of immunological reactions. G. S. Smith

3074. **Use of electrophoresis in combination with paper chromatography for identification of amino acids in hydrolysates of native proteins.** Yu. V. Galaev and E. K. Alimova (Lubenets) (Biochemistry Dept., Rostov Med. Inst.). *Biokhimiya*, 1956, **21** (5), 538–541.—The separation of amino acids, *e.g.*, from the lipoproteins of brain tissue, is carried out by paper chromatography with water-saturated phenol or butanol - acetic acid mixture as solvent, followed by electrophoresis for 6 hr. G. S. Smith

3075. **Polarographic determination of methionine.** F. Franěk (Res. Inst. of Food Technol., Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 243–248.—When treated with an excess of iodine - KI soln., methionine yields the corresponding periodide, the polarographic and oscillopolarographic behaviour of which has been studied. It yields at pH 8 (0·1 *M* $Na_2B_4O_7$ plus HCl) a well-developed polarographic wave of diffusion character ($E_{\frac{1}{2}} = -1{\cdot}05$ V *vs.* the S.C.E.), independent of pH. The reagent was 0·01 *M* iodine and 0·1 *M* KI; the excess of iodine can be removed by the addition of ascorbic acid. Under these conditions only tyrosine, histidine and cystine interfere. In the analysis of albumin hydrolysates, even 15 μg of methionine can be determined. The simultaneous determination of methionine and tyrosine was also developed. The oscillographic determination is suitable for 10^{-3} *M* soln. of methionine; in this case the excess of iodine need not be removed. J. Zýka

3076. **Bromatometric determination of methionine and cystine.** G. Vastagh and E. Varga (Staatl. Inst. für Hygiene, Budapest). *Pharm. Zentralh.*, 1957, **96** (3), 99–102.—A 5 to 10-ml aliquot from a freshly prepared 0·2% soln. (w/v) of methionine in 10% NaOH soln. is treated with 0·1 *N* $KBrO_3$ (10 ml) and KBr (0·40 g). After acidification with 15 ml of 10% HCl, water is added to give a final vol. of 50 ml. After 5 min., KI (0·5 g) is added and the iodine is titrated with 0·1 *N* $Na_2S_2O_3$. For the analysis of tablets, water is used instead of NaOH; the reaction takes 10 min., and starch and lactose do not interfere. Similarly, a 5-ml aliquot from a 0·2% soln. (w/v) of cystine in 1% NaOH, is added to 0·1 *N* $KBrO_3$ (10 ml) and KBr (0·5 g) and acidified with 10% HCl (10 ml). After 10 min., 0·5 g of KI is added and the iodine is titrated with 0·1 *N* $Na_2S_2O_3$. D. P. Felix

3077. **Quantitative determination of free and peptide-linked methionine as β-methylthiopropionaldehyde 2:4-dinitrophenylhydrazone.** A. Leismann and F. Turba (Staatl. Milchwirtschaftl. Lehr-und-Forschungsanstalt, Wangen im Allgäu, Germany). *Hoppe-Seyl. Z.*, 1957, **306** (4–6), 273–278.—Amino acids react quant. with ninhydrin with the formation of aldehydes; peptides do not react. Methionine forms an aldehyde which is volatile in steam. The reaction is carried out under reduced pressure, and the distillate is collected in 2:4-dinitrophenylhydrazine soln. to form the dinitrophenylhydrazone. When the soln. obtained by extracting the distillate with a mixture of equal vol. of benzene and heptane is applied to a column of $MgSO_4$ and eluted with the same solvent mixture, the pure β-methylthiopropionaldehyde phenylhydrazone (formed from methionine) is obtained. This can be estimated spectrophotometrically by measuring the extinction at 390 mμ. Recoveries of 92 to 106% are claimed for 20 to 134 μmoles of methionine. The other amino acids that form volatile aldehydes, *e.g.*, alanine, leucine, *iso*-leucine, phenylalanine and valine, can be determined by a similar procedure, but a column of zinc carbonate is used for chromatography. A simpler paper-chromatographic procedure with heptane - methanol [2:1 (v/v)] is described, but this does not distinguish between methionine and alanine. By carrying out the determination before and after hydrolysis the value for the peptide-linked methionine can be obtained. Neither salts nor sugars cause interference. Marking methionine with ^{35}S permits greater specificity than marking the carboxyl with ^{14}C, as then the determination of ^{35}S activity in the distillate is all that is required. F. Powell

3078. **The microscopic examination and identification of ergothioneine.** A. Kornhauser and M. Perpar (Inst. für organ. Chem., Univ. Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1957, (1), 80–84.—Crystals of ergothioneine formed from methanol, pyridine and methanol - ethyl acetate are examined by the Kofler thermo micro-methods. The m.p. is not sharp, decomposition with the formation of bubbles when the crystals are immersed in liquid paraffin begins at 150°. The eutectic temp. in *p*-acetamidosalol is 181° to 182° and in dicyandiamide 178° to 179°. Figures for the crystallographic constants and photomicrographs of the crystals obtained from these solvents are included.
P. S. Stross

3079. **Simple ultra-violet spectrophotometric method for the determination of protein.** W. J. Waddell (N. Carolina Univ. Med. Sch., Chapel Hill, N.C., U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (2), 311–314.—The rapid method described is based on the difference between the extinction at 215 mμ and at 225 mμ of a suitable dilution of the sample in 0·9% aq. NaCl. This difference multiplied by 144 gives the protein concn. in the diluted solution in micrograms per ml. Applications to the determination of total protein and albumin in plasma and to the determination of protein in cerebrospinal and pleural fluid are described. The method is not applicable to urine. W. H. C. Shaw

3080. **Variables involved in the fractionation of serum proteins by paper electrophoresis.** R. J. Henry, O. J. Golub and C. Sobel (Bio-Science Lab., Los Angeles, Calif., U.S.A.). *Clin. Chem.*, 1957, **3** (1), 49–64.—Rigid control of a number of variables is essential and a standardised procedure is proposed. Carry out the electrophoretic method normal to the apparatus employed, with barbitone buffer of pH 8·6 and Whatman 3MM paper for 16 hr. at 3·2 V per cm or 7 hr. at 5·8 V per cm. Heat-fix the strips at 107° ± 3° for 30 min. and stain for 6 hr. or overnight in bromophenol blue soln. (0·1 g of dye, 50 g of $ZnSO_4.7H_2O$ and 25 ml of 95% ethanol, diluted to 1 litre with 5% acetic acid). Wash in two changes of 5% acetic acid and fix in 5% acetic acid containing 0·3% of cryst. Na acetate. Blot the strips on absorbent paper and dry at 107°. Cut out the segments containing the protein fractions, place in test-tubes and elute with 6 ml of 0·01 *N* NaOH for 30 min. Read the colours at 540 mμ within 30 min. The trailing of the albumin was found to be const. with amounts of 100 to 600 μg, amounting to 1·4 μg per sq. cm of 3MM paper, and a correction is applied. H. F. W. Kirkpatrick

3081. **Chromatography of proteins on cellulose anion-exchangers using water - carbon dioxide systems.** M. A. Mitz and S. S. Yanari (Res. Div., Armour & Co., Chicago, Illinois, U.S.A.). *J. Amer. Chem. Soc.*, 1956, **78**, 2649–2650.—It has been found that proteins can be chromatographed on cellulose anion-exchangers in a system of water and CO_2. The proteins fractionated were free of small ions. *Procedure*—The protein, in water or dialysed against water, is equilibrated for 15 min. with the 2-(diethylamino)ethyl ether of cellulose (0·25 to 0·50 milliequiv. per g). The sorbate is separated by centrifuging, then washed and eluted with water kept in an atmosphere of CO_2. The exchanger is regenerated by washing with water. C. A. Slater

3082. **Turbidimetric titration of blood-serum proteins with salts of heavy metals.** S. A. Kibardin and T. N. Davydova) Pasteur Leningrad Scientific Res. Inst. of Epidemiology, Microbiology and Hygiene). *Lab. Delo*, 1957, **3** (1), 3–6.—The sample (0·2 ml) of serum is added to 1 ml of a buffer soln. (acetate - barbitone, pH 8·7) and diluted to 10 ml with water. The mixture is then titrated with a soln. of $CuSO_4.5H_2O$ or $ZnSO_4.7H_2O$ (25 mg per litre) added 5 ml at a time until 20 ml has been added. After each addition the extinction is measured through a green filter. The last measurement must be made not more than 4 to 5 min. after the first addition. The results in the form of graphs or tables showing extinctions at the four titration points are used for comparative purposes. G. S. Smith

3083. **Specific polarographic reaction of albumin. III. Quantitative investigation of the reaction between human serum albumins and some higher fatty acids.** K. Marha (Inst. Hyg. and Ind. Diseases, Prague, Czechoslovakia). *Chem. Listy*, 1957, **51** (2), 371–373.—Higher fatty acids and alcohols cause a decrease in the second part of the catalytic double wave of serum albumins, formed on the diffusion current of Co in aq. NH_3 soln. Fibrinogen, mucoprotein, γ-globulin and albumins isolated from eggs and cows' milk do not react in this way. The reaction can be used for the determination of higher fatty acids, even in admixture, and in 10^{-5} *M* concn., with an error $< \pm 5\%$. J. Zýka

3084. **Quantitative determination of the glucoprotein pattern of normal serum after electrophoretic separation on filter-paper.** C. B. Laurell and N. Skoog (Lab. Clin. Chemistry, Malmö Gen. Hosp., Sweden). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 21–25.—After electrophoresis the glucoprotein is stained by a periodate - Schiff method to give maximum colour and a clear background. The intensity of the stained bands was found to depend largely on the bisulphite concentration of the rinsing solution and on the amount of polysaccharide rather than on the type of polysaccharide bound to the protein. Quant. evaluation is effected by cutting up the strips and elution of the dye as follows. The cut paper fractions are incubated with 5 ml of *N* NaOH at 70° for 20 min. After removal and whilst the tubes are still warm, 5 ml of abs. ethanol is added, and the tubes are shaken and allowed to cool. One ml of acetic acid is then added and the colour read at 550 mμ against a water blank. The colour is stable for several hours. E. Kawerau

3085. **Chromatography of phosphatides on silicic acid impregnated paper.** G. V. Marinetti and E. Stotz (Rochester Univ. Med. Sch., N.Y., U.S.A.). *Biochim. Biophys. Acta*, 1956, **21** (1), 168–170.—Filter-paper impregnated with silicic acid by the method described is used for the ascending chromatography of phosphatides. Suitable solvents for one-dimensional chromatography are (*a*) di*iso*butyl ketone - acetic acid - water (40:30:7) and (*b*) *n*-butyl ether - acetic acid - chloroform - water (40:35:6:5). Two-dimensional chromatograms are developed first with chloroform - methanol (3 : 1) containing 2% of water or with solvent (*b*), then with solvent (*a*). The method requires 100 to 200 μg of phosphatides, and an application to the study of the metabolism of ^{32}P is described.
W. H. C. Shaw

3086. **Chromatographic micro-assay for cholesterol and cholesterol esters.** H. D. Wycoff and J. Parsons (Med. College of Georgia, Augusta, U.S.A.). *Science*, 1957, **125**, 347–348.—Mix 0·1 ml of plasma or serum with 5 to 7 ml of methanol - acetone (1 : 1), heat to boiling-point, cool, dilute to 10 ml with solvent and filter. Evaporate a 3-ml aliquot and transfer to a silicic-acid filled column (prep. described) with light petroleum (3 × 2 ml), forcing the liquid through at a rate of ⩾ 4 ml per min. Elute the esters with 4 ml of $CHCl_3$ - light petroleum (1 : 1), rinsing the tip of the tube with 1 ml of light petroleum. Elute the free cholesterol with 4 ml of methyl or ethyl acetate - light petroleum (1 : 1), forcing through until flow ceases and rinsing the tip of the tube as before. Evaporate the solvents and dissolve the fractions in 3·0 ml of warm glacial acetic acid; cool, add 2·0 ml of colour reagent, mix and read at 560 mμ. A standard containing 50 μg of cholesterol in 3·0 ml of acetic acid is treated similarly and a chromatographed solvent blank should also be run. The colour reagent is prepared by dissolving 1 g of $FeCl_3.6H_2O$ in 10 ml of glacial acetic acid, adding 10 ml of conc. H_2SO_4 to 1 ml of this soln., mixing, and diluting to 100 ml with conc. H_2SO_4.

H. F. W. KIRKPATRICK

3087. **Use of an organic base in the Zimmermann reaction.** A. M. Bongiovanni, W. R. Eberlein and P. Z. Thomas (Children's Hosp., Univ. of Pennsylvania, Philadelphia, U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1957, **17** (2), 331–332.—N-Benzyltrimethylammonium methoxide (**I**) has certain advantages as a substitute for KOH. It is stable for several months in soln., blanks are lower, development of atypical colour is less, and most supplies of abs. ethanol may be used without redistillation. **I** is supplied as a 40% soln. in methanol and this concn. gives max. sensitivity. The 17-oxosteroid residue is dissolved in 0·2 ml of abs. ethanol, 0·2 ml of ethanolic *m*-dinitrobenzene is added and the soln. is cooled in ice water. **I** soln. (0·3 ml) is added and the colour developed at 4° to 8° for 5 hr.; 1·0 ml of 50% ethanol is then added and the colour is read at 510 to 515 mμ.

H. F. W. KIRKPATRICK

3088. **Determination of urinary 11-oxygenated 17-ketogenic steroids.** H. H. Wotiz, H. M. Lemon and P. Marcus (Boston Univ. School of Med., Boston, Mass., U.S.A.). *J. Clin. Endocrin. & Metabolism*, 1957, **17** (1), 116–125.—The conjugated steroids are hydrolysed with β-glucuronidase and the extracts are treated with chromic acid to oxidise the 11-oxygenated steroids to androstane-3 : 11 : 17-trione and its isomer aetiocholane-3 : 11 : 17-trione. The triones are isolated by paper chromatography and measured quant. by the Zimmermann reaction. H. F. W. KIRKPATRICK

3089. **Determination of 17-hydroxycorticosterone [cortisol] in peripheral plasma from dogs and humans with radioactive *p*-iodophenylsulphonic acid anhydride (Pipsan).** E. Bojesen (Inst. Med. Physiol., Copenhagen). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 55–66.—The method is based on a variation of the isotope-dilution principle. Quant. esterification of cortisol is carried out under standardised conditions with "pipsan ^{35}S" (a preparation of pipsylglycine labelled with ^{35}S). Losses that invariably occur during extraction and purification of the steroid from plasma are allowed for by addition to the plasma of a known amount of the steroid labelled with ^{135}I which can be measured independently. It was found that the iodine activity in the indicator did not exchange with the sulphur activity of the reagent. The extracted steroids are separated from each other and from related compounds chromatographically, their relative position is determined by radio-autography and, after elution, the S to I ratio is measured with the counter. Mean recoveries of added steroid amounted to 86% over a range of 0·2 to 1·5 μg with a coefficient of variation of ± 6%.

E. KAWERAU

3090. **A micro-formaldehydogenic method for the analysis of chromatographic fractions of adrenal steroids.** A. M. Bongiovanni and W. R. Eberlein (Pennsylvania Univ., Philadelphia, U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (2), 320–323.—The method is based on oxidation with KIO_4, reduction of excess of KIO_4 with Na_2SO_3, and colorimetric determination of the formaldehyde with chromotropic acid. *Procedure*—To the dry steroid sample (2 to 30 μg) and standards (2 to 20 μg) add 0·1 ml of glacial acetic acid. Dissolve, add 0·4 ml of KIO_4 soln. (0·001 *M* in 0·3 *N* H_2SO_4) and allow to react for 45 min. at room temp. Add 0·10 ml of 10% aq. Na_2SO_3 and 1·0 ml of chromotropic acid soln. (500 mg of recryst. reagent in 4·0 ml of water; store at 4°; dilute 0·4 ml to 10·0 ml with conc. H_2SO_4 when required for use). Heat in a boiling-water bath for 30 min., cool, and measure the extinction at 560 mμ against a blank.

W. H. C. SHAW

3091. **Application of Zaffaroni-type partition systems to the paper chromatography of steroidal sapogenins.** A. J. McAleer and M. A. Kozlowski (Merck & Co., Inc., Rahway, N.J., U.S.A.). *Arch. Biochem. Biophys.*, 1956, **66** (1), 120–124.—Improved paper-partition chromatography of steroidal sapogenins is attained by descending development with (*i*) hexane - 2-(2-ethoxyethoxy)ethanol, (*ii*) *n*-heptane - formamide : methanol (1 : 1), (*iii*) *cyclo*hexane : benzene (1 : 1) - formamide : methanol (1 : 1) (*iv*) benzene - formamide : methanol (1 : 1) and (*v*) mixed octanes (boiling range 100° to 140°) - benzyl alcohol. Solvent system (*i*) is satisfactory for separating monohydroxy sapogenins, (*ii*) for monohydroxy keto-, (*iii*) for monohydroxy keto- and dihydroxy-, and (*iv*) for dihydroxy-sapogenins. System (*v*) can also be used for sapogenin acetates and permits higher loading of the chromatograms but gives poorer resolution. After drying for 1 to 2 hr. in air at 70° the sapogenins are detected on the chromatograms by spraying with a vanillin reagent (10 g in 100 ml of warm ethanol to which is added 100 ml of 85% H_3PO_4). The treated chromatogram is heated at 80° to 90° for 1 min. when all sapogenins appear as yellow spots, or for 10 min. when the characteristic colours listed are obtained. R_F values for 17 sapogenins in the five systems are given.

W. H. C. SHAW

3092. **Spectrophotometric determination of trypsin and trypsin inhibitors.** M. B. Rhodes, R. M. Hill and R. E. Feeney (Univ. of Neb., Lincoln, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 376–378.—The method is based on the determination of acid production by means of colour changes of an acid - base indicator; when a recording spectrophotometer is used, the enzyme activities may be obtained directly from the slopes of the transmittance - time curves. Trypsin concn. from 1 to 15 μg can be determined in a substrate - buffer - indicator soln. of 0·013 *M* toluene-*p*-sulphonylarginine methyl ester, 0·01 *M*

tri(hydroxymethyl)methylamine (pH 8·2) and 0·01% *m*-nitrophenol; the concn. range for inhibitors is 3 to 12 μg. The apparent reproducibility is within ± 5%. G. P. Cook

3093. **Comparative viscosimetric and turbidimetric determination of potency of commercial preparations of hyaluronidase.** K. O. Møller (Univ. Farmakol. Inst., Copenhagen). *Dansk Tidsskr. Farm.*, 1956, *Suppl.* 2, *Festskr. Svend Aage Schou*, 204–211.—Concordant results are obtained in comparisons of results for the potency of hyaluronidase determined by the viscosimetric method of Daubenmerkl (*Acta Pharm. Tox., Kbh.*, 1956, **12**, 65) and by the turbidimetric method of Dorfmann as modified by Daubenmerkl *et al.* (*Ibid.*, 1957, **13**, 1). Comparisons between the potencies of Scandinavian preliminary reference standard prep. and the international standard prep. show good agreement. Commercial prep. show a wide range of disagreement with declared potencies. P. S. Arup

3094. **Glucose oxidase with iodide - iodate - starch or o-tolidine as a specific spray for glucose.** L. M. White and G. E. Secor (U.S. Dept. of Agric., Albany, Calif., U.S.A.). *Science*, 1957, **125**, 495–496.—The air-dried chromatogram is sprayed with a soln. of glucose oxidase (1 mg per ml of Takamine Dee-O). After being set aside for 15 min. at room temp. it is sprayed with a freshly prepared aq. soln. containing 1% of soluble starch and 5% of KI, and then with a 5% aq. soln. of KIO_3. When the blue colour is fully developed, spraying with 5% aq. $NaHCO_3$ delays air oxidation of the background. An alternative test is to spray the chromatogram with a glucose oxidase - peroxidase reagent [dissolve 100 mg of Dee-O in 10 ml of acetate buffer (pH 5·3 to 5·6), add 1 g of scraped raw potato pulp, allow to stand 15 to 20 min. and filter through glass wool] and then immediately with a 1% ethanolic soln. of *o*-tolidine; the blue colour reaches a max. within a few min. and then gradually fades. H. F. W. Kirkpatrick

See also Abstracts 2881, 2995, 3019, 3004, 3020, 3096, 3174.

Drugs

3095. **Determination of morphine in poppy heads.** A. Bratina, M. Perpar and M. Tišler (Univ. Ljubljana, Yugoslavia). *Mikrochim. Acta*, 1957, (2), 167–173.—Morphine is chromatographically separated from accompanying materials by successively passing the aq. extract from the poppy heads through three ion-exchange columns. *Procedure*—Extract 5 g of finely ground ripe poppy heads (stalks and seeds having been removed), on which the water content has been previously determined, with 200 ml of water in a Soxhlet apparatus for 5 hr. Filter the extract and make up to 250 ml with H_2O. Pass 50 ml of this soln. through the following previously prepared micro columns, filled with an aq. suspension of the resins to a height of 5 to 6 cm—(*i*) Zerolit (with 2% of divinylbenzene) (H form), (*ii*) De-Acidite FF (OH form), (*iii*) Zerolit (with 2% divinylbenzene) (Na form). When the 50-ml aliquot has passed through (*i*), wash with 5 ml of de-ionised water and then elute with 0·5 *N* of aq. NH_3 (50 ml). Pass the eluate through (*ii*), wash with 5 ml of de-ionised water and elute with *N* acetic acid (50 ml). Add *N* HCl (1 ml); evaporate to dryness on a water bath. Dissolve the residue in 10 ml of water and pass through (*iii*). Wash with 5 ml of water and then with 50 ml of borate buffer soln. (pH 8·6). Reject the eluate and then elute with borate buffer soln. (pH 9·4) (250 ml) and add 3 *N* HCl (3 ml). Evaporate the eluate to ≃ 30 ml on the water bath, prepare the nitroso derivative (*cf.* Adamson and Handisyde, *Analyst*, 1945, **26**, 1061), and make up to 50 ml with water. Measure a 10-ml aliquot on the Lange Universal absorptiometer (1-cm cell and BG-7 filter). A calibration curve for morphine contents from 0 to 80 μg per ml obeys Beer's law. Recoveries of 98% of morphine were obtained; these results agreed with those obtained by the Van Etten procedure (*cf. Anal. Abstr.*, 1956, **3**, 3167). D. F. Phillips

3096. **Analysis of atropine and its hydrolytic products by filter-paper chromatography.** H. Schriftman and A. A. Kondritzer (Chemical Warfare Lab., Army Chem. Center, Md., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (3), 173–176.—Micro quantities of atropine (**I**) can be extracted from biological material with > 90% recovery by a procedure which involves homogenisation with 5% trichloroacetic acid, basification and extraction with $CHCl_3$. **I** can be separated from tropine (**II**) by descending paper chromatography with the alcoholic phase of *n*-butanol - conc. HCl - H_2O (5:1:3); the R_F values are **I** 0·95, **II** 0·70. The bases can be determined by spraying the developed chromatogram with a modified Dragendorff reagent and scanning with a densitometer at 530 mμ (for **I**) or 570 mμ (for **II**). Beer's law is obeyed in the range 2 to 25 μg. **I**, **II** and tropic acid (**III**) in 10 to 100-μg quantities can be separated by paper chromatography with the upper phase of *n*-butanol - acetic acid - H_2O (10:1:6); the R_F values are **I** 0·58, **II** 0·41, **III** 0·86. Spray with a 0·01% soln. of bromophenol blue in $1·5 \times 10^{-4}$ *N* NaOH. **I** and **II** immediately show as deep-purple spots and **III** appears as a yellow spot which slowly increases in intensity. For quant. results, scan at 570 mμ (for **I** and **II**) or 440 mμ (for **III**). A. R. Rogers

3097. **The chromatographic separation of cocaine hydrochloride and its probable metabolites, benzoylecgonine and ecgonine: quantitative densitometry.** V. Castañeda and J. Chiriboga. *Bol. Soc. Quim. Peru*, 1956, **22**, 214–220.—Ascending chromatography at room temp. for 22 hr. on Whatman No. 1 paper, followed by air drying and spraying with Dragendorff reagent, was used to separate cocaine, benzoylecgonine and ecgonine as hydrochlorides, and develop orange, rose-orange and salmon-pink spots, with R_F values of 0·51, 0·11 and 0·05, respectively. The best solvents were (*i*) *n*-butanol, acetic acid, water (100:4:50), and (*ii*) *n*-butanol, acetic acid, water (50:8:50), from either of which, after mixing in a tap-funnel and standing for 24 hr., the aq. phase was discarded. Before obtaining standard graphs with a Beckman spectrophotometer, elution with various solvents was tried, including dil. HCl, but extraction was poor. For cocaine, 1 to 11 μg, for benzoylecgonine 2 to 10 μg, and for ecgonine 10 to 100 μg, were used. The Dragendorff reagent background disappeared from the paper 24 hr. after development. The sensitivities were: cocaine 1 μg, benzoylecgonine 4 μg, ecgonine 10 μg. R. L. Mortlock

3098. **Spectrophotometric determination of strychnine in Easton's syrup.** S. Z. Patel and B. S. Gandhi (Alembic Chemical Works Co., Baroda, India). *Indian J. Pharm.*, 1957, **19** (2), 37–40.—The orange - red colour that strychnine (**I**) gives with Mandelin's reagent may be used for the rapid determination of **I** in Easton's syrup. The quantity of quinine normally present does not significantly interfere. The recovery is > 90%. *Procedure*—Extract the total alkaloids from the sample (50 g) by the method of the B.P.C. 1954. Take up the residue of **I** and quinine in dil. H_2SO_4 (100 ml) and filter if necessary. Mix a 1-ml aliquot (containing 40 to 100 μg of **I**) with 0·05% (w/v) ammonium vanadate in 65% (v/v) H_2SO_4 (5 ml). After 2 min., add water (4 ml) and mix well. After a further 10 min., measure the extinction at 530 mμ against a reagent blank. A. R. ROGERS

3099. **Determination of protoveratrine. II. Separation of protoveratrines A and B from associated alkaloids.** J. Levine and H. Fischbach (F.D.A. Dept. of Health, Educ. and Welfare, Washington, D.C., U.S.A.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1957, **46** (3), 191–192.—The procedure described previously (*cf. Anal. Abstr.*, 1956, **3**, 1481) does not always give quant. separation of protoveratrine A (**I**) and protoveratrine B (**II**) and a modified procedure is now given. The separations can be monitored by chromatography on paper distinctly moist with buffer, pH 3·5, with the solvent system 2-ethoxyethyl acetate - 1:2-dichloroethane - pyridine (10:15:1) as mobile phase; the R_F values are **I** 0·7, germitetrine 0·5, **II** 0·25. *Procedure*—Prepare a column of acid-washed Celite (2 g) on which is incorporated a mixture (2:1) (2 ml) of buffer (pH 3·0) and ethanediol. Add a soln. of the sample (2 to 5 mg) in benzene or CCl_4. Elute in the following sequence: a mixture of CCl_4 (90 ml) and 1:2-dichloroethane (60 ml); 1:2-dichloroethane (100 ml); a mixture of 1:2-dichloroethane (50 ml) and $CHCl_3$ (100 ml); $CHCl_3$ (100 ml). The first fraction elutes **I** quant. and **II** is eluted in the third fraction. A. R. ROGERS

3100. **Determination of glycoalkaloids of potato and their separation.** V. A. Paseshnichenko and A. R. Guseva (A. N. Bakh Inst. of Biochem., Acad. Sci. U.S.S.R., Moscow). *Biokhimiya*, 1956, **21** (5), 585–590.—The determination of potato glycoalkaloids (solanine and chaconine) is carried out by paper chromatography with ethyl acetate - acetic acid - water (11:2:2), followed by development with Alberti's reagent (2 ml of conc. H_2SO_4 and 1 ml of 1% formaldehyde soln.). G. S. SMITH

3101. **The biological assay of penicillin V. II.** R. Brunner (Forschungslab., Biochemie G.m.b.H., Kundl, Tirol). *Sci. Pharm.*, 1956, **24** (1), 1–4.—The U.S. Food and Drug Administration has defined the unit of activity of penicillin V (**I**) so that equimolecular amounts of **I** and penicillin G (**II**) contain the same number of units. Preparations containing **I** should, however, always be assayed against a pure standard of **I**, because **I** is more active against many organisms than is **II**. In the iodimetric titration of **I**, the empirical factor of 600 units per ml of 0·01 *N* iodine may be used. A. R. ROGERS

3102. **Use of the recording biophotometer for the control of penicillin content of pharmaceutical preparations.** S. Lambin, A. German and A. Desvignes (Lab. de Microbiol., Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1956, **14** (5), 352–366.—The conditions for max. sensitivity of the assay of penicillin depending on the growth of cultures of *Staphylococcus aureus* (strain 101) are investigated with a Bonèt-Maury and Jouan biophotometer, on which the transmissions of six cells can be simultaneously recorded. Optimum conditions are obtained with 25-mm cells, 8-hr. cultures containing 5×10^6 bacteria per ml and additions of penicillin of 0·017 to 0·0185 unit per ml. E. J. H. BIRCH

3103. **Ion-exchange chromatography of streptomycin on Permutit.** S. E. Bresler and G. V. Samsonov. *Kolloid. Zhur.*, 1956, **18** (2), 155–157; *Ref. Zhur., Khim.*, 1956, Abstr. No. 72,065.—For the chromatographic purification of streptomycin (**I**) from organic impurities, Permutit is used as adsorbent. The adsorption of **I** on Permutit proceeds with the formation of a sharp front. Displacement is carried out with a 20% soln. of NaCl. During this process there is a sharpening of the front and the formation of a stationary zone. At low concn. of the displacing ion the zone of **I** is washed out. C. D. KOPKIN

3104. **Chemical methods for the determination of antibiotics. VI. Colorimetric determination of erythromycin.** Keiichiro Kakemi, Toyozo Uno and Hajime Yamashina (Pharm. Dept., Med. Fac., Kyoto Univ., Sakyo-ku, Kyoto). *J. Pharm. Soc. Japan*, 1956, **76** (10), 1116–1118.—When erythromycin (**I**) is hydrolysed by standing for 30 min. at 25° in dil. H_2SO_4, then made alkaline, heated for 5 min. at 100° and extracted with $CHCl_3$, the extract, on shaking with a satd. aq. soln. of H_3BO_3 and methyl orange, develops a yellow colour in the $CHCl_3$ layer; if this is separated and shaken with *N* H_2SO_4 a red acid layer is produced with max. extinction at 508 mμ. If the acid hydrolysis is omitted, pure **I** gives no colour but its natural decomposition products do. The difference in the colour produced is a measure of the **I** present. The values obtained agree fairly well with the bioassay. K. SAITO

3105. **Clinical and laboratory assessments of senna preparations.** J. C. McClure Browne, V. Edmunds, J. W. Fairbairn and D. D. Reid (Hammersmith Hosp., London). *Brit. Med. J.*, 1957, 436–439.—Chemical, biological and controlled clinical trial methods of determining the potency of various senna prep. showed general agreement in results. Liquid prep. vary greatly in potency and are subject to deterioration; a dry granular prep. proved stable and potent. H. F. W. KIRKPATRICK

3106. **Experience of the microbiological assay of vitamins and amino acids by large-plate methods.** J. S. Simpson and D. F. Harris (Glaxo Lab. Ltd., Greenford, England). *Analyst*, 1957, **82**, 210–211.—A comparison of the large-plate method with the Petri-dish method has confirmed the superiority of the former method for antibiotics, vitamin B_{12}, etc., and also for other water-soluble vitamins and amino acids. A (2 + 2) design has been employed, usually of the 8 × 8 quasi Latin-square type accommodating six samples and two standards. Results of the determination of riboflavine in five samples by the tube and large-plate assays are quoted. The max. deviation of any single result expressed as a percentage of the mean is ± 16% for the tube assay and ± 7% for the large-plate assay. A. O. JONES

3107. **The use of Kofler micro-methods in the analysis of drugs. III. Quantitative analysis of binary mixtures.** A. Sekera and J. Pokorný (Pharm. Chem. Inst., Masaryk Univ., Brünn, Czechoslovakia). *Mikrochim. Acta*, 1957, (1), 103–112.—The Kofler micro-refractometric method was used for determining the composition of 19 binary mixtures of pharmaceuticals. Mixtures of acetylsalicylic acid with phenacetin, caffeine with phenacetin or acetanilide, amidopyrine with barbitone, phenobarbitone, allobarbitone or phenacetin, phenobarbitone with bromvaletone, and santonin with phenolphthalein could be analysed over the whole range of concn. Various other combinations of these drugs and of phenyl salicylate, codeine phosphate, quinine hydrochloride, papaverine hydrochloride, hexamine, urea and piperazine could be analysed over a part of the range of concn. The method is not applicable to some mixtures. Tables of the refractive indices of the various mixtures over a range of temp. are given. P. S. Stross

3108. **Spectrophotometric study on 5:5-diphenylhydantoin.** I. Bjørge, J. Presthus and K. F. Støa (Biochem. Lab., Univ. Clinic, Bergen, Norway). *Medd. Norsk Farm. Selsk.*, 1957, **19** (2), 17–22 (in English).—5:5-Diphenylhydantoin (**I**) may be assayed by the increase of u.v. absorption in alkaline soln. *Procedure*—Measure the extinction at 233 mμ of a 0·001 to 0·003% soln. in 96% ethanol in a 1-cm cuvette. Add 0·3 *N* NaOH (0·02 ml) directly to the soln. in the cuvette, stir, and again read the extinction. The concn. of **I** in mg per 100 ml = 6·00 ΔE. A. R. Rogers

3109. **A rapid, simple and accurate method for the determination of sulphonamides.** Lee Kum-Tatt (Gov. Chem. Dept., Outram Road, Singapore). *Analyst*, 1957, **82**, 185–188.—A volumetric method has been developed for the determination of seven of the most common sulphonamides. It is applicable only to those that form insol. silver salts with $AgNO_3$. The sample (≃ 200 mg) is dissolved in warm acetone, then $Na_2Cr_2O_7$ and MgO are added and the mixture is titrated with 0·05 *N* $AgNO_3$ until a permanent red colour appears. In a gravimetric procedure, the soln. in acetone is treated with a large excess of 0·1 *N* $AgNO_3$ and the mixture is heated on a water bath for 30 min. The pptd. silver salt is collected, washed, dried and weighed. The excess of $AgNO_3$ in the combined filtrate and washings is determined by the Volhard method. Mixtures of any one of the sulphonamides tested with sulphanilamide or sulphaguanidine (which do not react with $AgNO_3$) can be analysed by determining the "acid sulphonamide" by titration with $AgNO_3$ and then the total sulphonamide content by the method of the B.P. 1953. For mixtures with sulphacetamide (also non-reactive), the gravimetric method or the back-titration method must be used. Quoted results indicate satisfactory accuracy. The method is applicable to tablets containing the normal excipients. A. O. Jones

3110. **Colorimetric method for the determination of small amounts of dienoestrol and stilboestrol.** G. Tokár and I. Simonyi (United Pharm. and Foodstuff Factory, Budapest). *Magyar Kém. Foly.*, 1956, **62** (10), 329–331.—The nitrated derivatives of dienoestrol (**I**) and stilboestrol (**II**) give an intense yellow colour with alkali. The Beer-Lambert law is obeyed. All colorimetric determinations (including the blanks) were carried out in a Pulfrich photometer, with a 1-cm cell and an S42 filter. *Procedure*—Evaporate an alcoholic or aq. alcoholic soln. of **I** (1 to 5 ml, containing 30 to 80 μg) to dryness. Moisten the residue with 0·5 ml of nitrating mixture (1% KNO_3 in conc. H_2SO_4) and maintain, with occasional stirring, at room temp. for 20 min. or at 60° for 15 min. Add H_2O (1 ml) and 10% NaOH (7 ml). After 30 min., wash the soln. with 10% NaOH soln. into a graduated test-tube, dilute to 9 ml with the same solvent, and measure the extinction. To an aliquot containing the diacetate of **I** (50 to 80 μg) add 0·1 *N* NaOH (1 ml) and evaporate to dryness. Treat the residue as above. **II** (40 to 60 μg) is determined in the same way as **I**, but its coeff. of extinction varies slightly with the temp. For determination in tablets, dissolve a sample containing **I** (≃ 500 μg) in hot ether (5 × 5 ml), filter and evaporate to dryness. Take up the residue in 10% NaOH soln. (0·5 ml) and H_2O (5 ml), and dilute to 50 ml with water. Determine **I** as described above. For **II** (as dipropionate), add *N* NaOH (1 ml) before evaporation. For the determination of **I** in oily injections, dissolve the sample containing **I** (500 to 600 μg) in ether, extract it with *N* NaOH (3 × 10 ml) and, after driving off the ether, dilute with water to 50 ml. Determine **II** similarly, but with methanol for the extraction. A. G. Peto

3111. **Rapid colorimetric determination of thiosinamine.** S. Z. Patel and H. M. Mody (Alembic Chemical Works Co., Baroda, India). *Indian J. Pharm.*, 1957, **19** (2), 34–37.—Grote's reagent as modified by Olsen *et al.* (*J. Biol. Chem.*, 1947, **169**, 681) gives a green-blue colour with thiosinamine (**I**) in the cold at pH 6·8, which may be used for the rapid determination of **I** in ointments or injection soln. The recoveries of **I** from five ointments containing also Na salicylate and ethylmorphine hydrochloride ranged from 100·5 to 102%. A. R. Rogers

See also Abstracts 2993, 3012, 3015, 3019, 3065, 3076.

Food

3112. **Determination of traces of lead in organic materials. A visual mixed-colour process with dithizone.** F. Neumann (Forschungslab. der Zellstoff-Fabrik Waldhof, Mannheim-Waldhof). *Z. anal. Chem.*, 1957, **155** (5), 340–349.—In a colorimetric determination of traces of Pb in foodstuffs and other organic materials, based on treatment with dithizone (**I**), the mixed colour of the mixture of **I**-Pb compound and soln. of free **I** in $CHCl_3$ changes from pure green through bluish-green and bluish-red to pure red, with increasing concn. of Pb. By visual comparison with standards, 3 to 8 μg of Pb was determined to within 0·1 to 0·2 μg, an error of 4%. This error can be reduced if a spectrophotometer is used, but this method has disadvantages and is time-consuming for routine analyses. **I** is not a specific reagent for Pb, but interference from other metals can be eliminated by the use of masking agents. Bismuth is an exception, but may be removed by prior extraction of the test soln. with **I** in CCl_4. W. J. Wright

3113. **Determination of lead and copper in organic materials (foodstuffs) by a dry-ashing procedure.** D. Abson and A. G. Lipscomb (John Mackintosh & Sons Ltd., Halifax, Yorks., England). *Analyst*, 1957, **82**, 152–160.—Methods for the dry-ashing of

samples before the determination of Pb and Cu are examined and a method suitable for a wide range of food materials is developed. The sample is heated with H_2SO_4 to a brittle charred mass, which is then powdered (if necessary) and re-heated until free from H_2SO_4. The residue is evaporated with an aq. suspension of $MgCO_3$ and the ashing is completed below 550°. If the final ash is bulky, the treatment with $MgCO_3$ is unnecessary. The ash is dissolved in dil. HCl and the soln. is filtered. If considerable amounts of $CaSO_4$ are formed the ash is boiled gently for 1·5 hr. with 5% Na_2CO_3 soln. before solution in HCl. To determine Pb, an aliquot portion is treated with citric acid and sodium hexametaphosphate soln., and neutralised with aq. NH_3, then KCN and hydroxylamine hydrochloride are added and the Pb is extracted with a chloroform soln. of dithizone. To determine Cu, another aliquot is warmed with dil. HCl and KI soln., the liberated iodine is removed with $Na_2S_2O_5$ soln. and the Cu is extracted with diethylammonium diethyldithiocarbamate soln. The extinctions of the extracts are measured and referred to calibration graphs. A. O. JONES

3114. **The determination of methyl bromide adsorbed by foodstuffs treated with this insecticide.** P. Desbaumes and J. Deshusses (Lab. Cantonal de Chimie, Geneva). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (6), 550–561.—The foodstuff is heated to 70° and the methyl bromide is swept out by a current of air, passed through a quartz tube at 1000° and the gaseous decomposition products are absorbed in alkaline H_2O_2. The Br^- are determined with $AgNO_3$ by the method of Bognar and Veresköi (*Anal. Abstr.*, 1955, **2**, 1427). M. F. C. LADD

3115. **Detection and determination of hydroxymethylfurfuraldehyde in honey and artificial honey.** C. Franzke and H. Iwainsky (Inst. f. Lebensmittelchemie und -technol. der Humboldt-Univ., Berlin). *Fette, Seif., Anstrichmitt.*, 1956, **58** (10), 859–862.—Hydroxymethylfurfuraldehyde (**I**) in artificial honey is determined by measuring the absorption spectrum of an aq. soln. over the range 240 to 320 mμ; **I** shows a sharp maximum at 282·5 mμ ($E^{1\%}_{1cm}$ = 1300). Irrelevant absorption is assumed to be linear over the range considered. In 19 samples of artificial honey, the content of **I** varied from 0·008% to 0·141%. All the samples gave a positive Fiehe reaction. No **I** could be detected in 11 samples of fresh natural honey. When natural honey is heated to 100° for 1 hr. a detectable amount of **I** is produced, and heating for 5 hr. raises the content of **I** to 0·06%. Ethyl acetate is the best solvent to use for the extraction of **I** for the colorimetric Fiehe test, but it also extracts some fructose. In a paper-chromatographic method for the detection of **I**, butanol - ethanol - water (2:4:1) is used as a solvent mixture with S. & S. No. 2040b paper. The spots are indicated by spraying the paper with resorcinol - trichloroacetic acid reagent. The chromatogram is run for 5 hr. by the ascending technique. As little as 2 μg of **I** can be detected on the paper. E. HAYES

3116. **The jelly-strength grading of pectins for use in jam manufacture.** M. Olliver, P. Wade and K. P. Dent (Chivers and Sons, Ltd., Histon, Cambs., England). *J. Sci. Food Agric.*, 1957, **8** (3), 188–196.—The grade of rapid-setting pectin powders is elevated by the addition to samples under laboratory test of a surface-active agent. Saponins react similarly. It was found that a reliable indication of the grade of a pectin and its behaviour under production conditions could be assessed by modification of the acid-in-boil method of the B.F.M.I.R.A. Before the soluble-solids content of the boil reached 60%, a soln. of Teepol 530 (or 410) (10% v/v) (5 ml per kg of gel) was added. The source of sugar used was immaterial, but some liquid pectins with setting-points $> 90°$ gave anomalous results (*cf. Analyst*, 1957, **82**, 127). D. G. FORBES

3117. **The amino-carbonyl reaction of milk products. II. Direct colorimetric determination of urea in milk.** Susumu Adachi (Lab. of Animal Products Tech., Fac. Agric., Tohoku Univ., Sendai). *J. Agric. Chem. Soc. Japan*, 1956, **30** (2), 126–131.—Archibald's colorimetric determination of urea (in blood) with α-oximinopropiophenone (**I**) (*J. Biol. Chem.*, 1945, **157**, 507) was applied to its determination in condensed milk. The colour produced from urea and **I** in an acid soln. is stable under diffused light, but rapidly fades in sunlight. The working curve is linear for 10 to 80 mg per 100 ml. The results agree well with those obtained by the urease method. *Procedure*—The sample (1 ml) is mixed with water (7 ml) and Somogyi reagent (2 ml) (*J. Biol. Chem.*, 1930, **86**, 655) and centrifuged, and a 2-ml portion of the supernatant liquid is treated with water (5 ml), a mixture of H_2SO_4, H_3PO_4 and H_2O (1 + 3 + 1) (5 ml) and 4% **I** soln. (0·4 ml) and the colour determined spectrophotometrically at 540 mμ. K. SAITO

3118. **Biochemistry of cheese ripening. XIX. Determination and characterisation of prolidase in sour milk cheese.** J. Schormüller and H. Müller (Inst. für Lebensmittelchemie und Lebensmitteltechnol., Tech. Univ., Berlin-Charlottenburg, Germany). *Z. LebensmittUntersuch.*, 1957, **105** (1), 39–51.—Prolidase has a pH optimum of 7·75 and is relatively heat-sensitive. It is activated considerably by Mn^{2+} and inhibited strongly by Ag^+, Hg^{2+}, and organomercury compounds, and also by Cd^{2+}, differing, in this respect, from prolinase which is activated strongly by Cd^{2+}. In normal cheese, the prolidase activity increases to the end of the ripening stage and decreases after $\simeq$ 11 days. Its activity in sour milk cheese is of essential significance for the proteolytic breakdown of cheese protein. S.C.I. ABSTR.

3119. **Determination of the "butyric acid number" of butter.** G. Cerutti and A. Tamborini (Ist. di Ind. Agrarie, Univ. Milano, Italy). *Ann. Sper. Agr.*, 1956, **10**, 447–450.—Various typical data have been determined for fats of several plant and animal sources liable to be employed as adulterants of butter. The butyric acid no. (*cf.* Grossfeld, *Z. LebensmittUntersuch.*, 1938, **76**, 123) of all the Italian butters examined, except that of a winter butter from Mantua, lay between 20 and 22. Only dolphin fat gave a value of about 22, all the other fats gave values of < 2, and lard gave 0. Values varying from 15·8 to 19·7 are given for mixtures of pure butter with 5 or 10% of various adulterants, and it is suggested that a value of $< 19·5$ should be regarded as an indication of adulteration. The method is sufficiently delicate to detect 5% of adulterant. P. HAAS

3120. **Critical review of different methods for estimating butter fat in the presence of coconut oil.** H. Hadorn and H. Suter (Lab. VSK, Basel). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (6), 512–535.—Of the several methods tested, that of Grossfeld (*Z. Untersuch. Lebensmitt.*, 1926, **51**, 203) is the most satisfactory for the semi-micro determination of butyric acid and residual numbers (*cf. Z. Untersuch. Lebensmitt.*, 1932, **64**, 446) in coconut oil.

M. F. C. LADD

3121. **A simplified method for the estimation of water, fat and starch in margarine.** G. Lindstedt (State Inst. of Public Health, Tomteboda, Sweden). *Mitt. Lebensmitt. Hyg., Bern*, 1956, **47** (6), 506–511.—The method of Wachsmuth (*J. Pharm. Belg.*, 1947, **2**, 172) for estimating water and fat in margarine has been modified. A colorimetric method for determining starch is described. The complete analysis requires 1 g of margarine and the method is rapid and accurate.

M. F. C. LADD

3122. **Detection of refined lard.** H. P. Kaufmann, J. G. Thieme and F. Volbert (Dtsch. Inst. für Fettforschung, Münster, Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (7), 505–506.—An attempt is made to distinguish genuine lard from samples that have been treated with bleaching-earth by comparing the absorption spectra of the two materials, determined in hexane, over the range 200 to 320 mμ. For genuine lard, the ratio $E_{232/268}$ is within the range 18 to 24 and does not change with the development of rancidity; for lard that has been treated with bleaching-earth, the ratio is within the range 7 to 10.

E. HAYES

3123. **Detection of refining of lard. II. The u.v. absorption spectrum.** H. P. Kaufmann, J. G. Thieme and F. Volbert (Dtsch. Inst. für Fettsorschung, Münster Westf., Germany). *Fette Seif., Anstrichmitt.*, 1956, **58** (11), 995–996.—When lard is refined with bleaching earth, the extinction at 268 mμ in hexane soln. increases owing to the presence of a triene structure. The characteristic triene structure can usually be recognised when values of log $E_{1\,cm}^{1\%}$ are plotted against wavelength. A more certain indication is obtained by measuring values of $E_{1\,cm}^{1\%}$ at 264, 268 and 272 mμ and calculating "*T*-values" and "*Q*-values," where

$$T = [E_{268} - (E_{264} + E_{272})/2] \times 100$$

and $Q = T/E_{268}$.

If $T > 1$ and $Q > 7$, refined lard is present. For values of Q from 4 to 7, small amounts of refined lard may be present, but the spectroscopic evidence is not conclusive. (*Cf. Anal. Abstr.*, 1957, **4**, 1346.)

E. HAYES

3124. **Determination of traces of mercury in apples.** D. C. Abbott and E. I. Johnson (Gov. Lab., Clement's Inn Passage, London). *Analyst*, 1957, **82**, 206–208.—The diced sample (50 g) is treated by a wet-ash procedure with a selenium catalyst in an apparatus which has provision for the addition of extra HNO_3 in the early stages and H_2O_2 towards the end of the digestion, and a reflux air-condenser surmounted by a water condenser. The cooled liquid, diluted with the washings of the condensers, is filtered and the filtrate is adjusted to 250 ml. The acidity (determined by titration of 1 ml) is reduced to 1 *N* with aq. NH_3 and the liquid is extracted with a chloroform soln. of dithizone in the presence of hydroxylamine hydrochloride soln. The extract is shaken with 0·1 *N* HCl and hydroxylamine hydrochloride soln., $Na_2S_2O_3$ is then added and, after shaking, the chloroform layer is discarded. The liquid is then shaken with NaOCl soln., hydroxylamine hydrochloride soln. is added, the shaking is repeated and the liquid is extracted twice with chloroform, the extracts being discarded. Acetic acid and dithizone soln. are added and the extinction of the dithizone extract is measured against chloroform at 490 mμ and referred to a standard graph. Recovery of Hg, added as phenylmercury chloride, was 94%.

A. O. JONES

3125. **Detection of synthetic flavours, chicory and caramel in coffee extracts.** H. van den Dool. *Ann. Falsif.*, 1957, **50**, 23–29.—A modification of the method of Séris (*Ibid.*, 1954, **47**, 26) is described. Coffee extract (0·5 g) is dissolved in 5 ml of ethanol (30%, v/v), shaken for 2 min. with 5 ml of *cyclo*hexane, then centrifuged, and the *cyclo*hexane layer is transferred to a 10-ml calibrated flask. After a second extraction with *cyclo*hexane, the combined extracts are made up to vol., and the u.v. absorption spectra examined. It is shown that the criteria of Séris, depending on the presence or absence of certain peaks on the absorption curves, are valid only in special cases. For pure coffee extracts the author finds that under his conditions the relationship $E = (3{\cdot}4 + 0{\cdot}28\,m) \pm 2{\cdot}0$ holds for E, the coeff. of extinction at 275 mμ, and m, the percentage of dry matter in the extract, measured refractometrically. This line is plotted with E as ordinate and m as abscissa, and if the observed figures for any extract give a point lying above the line, synthetic flavour is present, and points lying below the line suggest the presence of caramel or chicory. Figures and curves are given for pure and commercial coffee extracts, chicory, caramel, synthetic flavour (mercaptan type), and a steam-distillate from coffee. Attempts to detect these additions by means of paper chromatography were unsuccessful.

R. E. ESSERY

3126. **Refractometric analysis of beer. Development of calculated formulae for alcohol and actual extract from the refractive index and the specific gravity of beer. II.** E. Schild and G. Irrgang (Inst. für chem.-tech. Analyse, Weihenstephan, Germany). *Brauwissenschaft*, 1957, **10** (1), 19–24.—Data are given on 35 beer samples analysed by distillation and refraction processes. Two fundamental equations, forming the basis for development of formulae, are discussed: (*i*) The sp. gr. of a beer is equal to the sum of the sp. gr. of the dealcoholised portion and of the alcoholic distillate (both made up to original vol.) minus 1. (*ii*) The refractive index of a beer is the sum of the indices of the de-alcoholised portion and of the alcoholic distillate (both made up to original vol.) minus the refractive index of distilled water. Tests made within the limits of full beer and strong beer indicated a close correspondence between the calculated and the actual values.

S.C.I. ABSTR.

3127. **Determination of *iso*humulone and its analogues in beer.** G. A. Howard and A. R. Tatchell (Brewing Industry Research Foundation, Nutfield, England). *J. Inst. Brewing*, 1957, **63** (2), 142–153.—From a study of four extraction-spectrophotometric and three countercurrent distribution methods it is shown that the efficiency of different extraction procedures varies, and that the

ratio of extracted contaminants to true bittering substances (*iso* compounds) varies with the analytical procedure and with the type of hop and the brewing procedure employed. It is therefore necessary to ensure complete extraction and also complete removal of contaminants; this has largely been achieved by the "quick countercurrent method" of Rigby and Bethune (*cf. Anal. Abstr.*, 1956, **3**, 250) and by the following method. The degassed beer (800 g) is mixed with conc. HCl (50 ml) and pepsin (50 mg) and allowed to stand for 1 hr. It is then extracted four times in a specified manner with light petroleum (boiling range 40° to 60°, 60 ml), emulsions being broken by centrifuging at 3000 r.p.m. for 7 to 10 min. The petroleum extract is freed from contaminants by washing (3 × 10 ml) with acidified methanol [methanol - 4 *N* HCl (6·8:3·2, v/v)] and then from acid by washing with water, and the *iso* compounds are extracted into 2 *N* NaOH until the alkaline layers are colourless (total 3 ml). An aliquot (0·1 ml) of the alkaline extract is diluted suitably and the extinction is read at 255 mμ for total *iso* compounds (extinction coeff. 520). The remainder is treated with 30% aq. H_2O_2 (2 ml) at 0° overnight, excess of H_2O_2 is removed on the water bath, the cooled solution is treated with anhydrous $KHSO_4$ (15 g in a column 10 cm × 1·4 cm), the liberated fatty acids are extracted with anhydrous ether and analysed by the gas-chromatographic method of Howard and Tatchlel (*J. Inst. Brewing*, 1956, **62**, 20). The gas-chromatographic method is more rapid and convenient than the countercurrent distribution one, the main limitation on speed being the initial extraction procedure. The authors discuss the nature and influence on the analysis of the contaminants, methods of calculation from countercurrent distribution patterns, and the utilisation of humulone analogues during brewing.

R. E. Essery

3128. **Analysis of hop oil by gas - liquid partition chromatography.** F. L. Rigby and J. L. Bethune (Canadian Breweries Res. Div., Toronto). *J. Inst. Brewing*, 1957, **63** (2), 154–161.—A laboratory-made apparatus is described that is suitable for column temp. up to 200°. The heating jacket consists of a 6-ft. length of 1½-in. copper piping wrapped with asbestos and wound with nichrome wire, temp. being controlled by a Variac transformer. The column tubing is of 6-mm Pyrex glass, and emerging vapours are detected by a thermal conductivity cell and Wheatstone bridge, the out-of-balance signal being recorded on a moving chart. For whole oils, the column was packed with a mixture (70:30) of Celite and Dow Corning high-vacuum silicone stopcock grease, with a similar mixture of crushed diatomaceous earth firebrick and Apiezon M high-vacuum stopcock grease for oxygenated fractions. Hydrogen was used as carrier gas, since nitrogen gives low sensitivity. Whole oils were obtained by steam-distillation, and the oxygenated fractions were separated by adsorption on silicic acid. Up to 13 peaks are obtained in chromatograms of whole oils, about 95% being accounted for by myrcene, humulene, methyl nonyl ketone, and β- and γ-caryophyllene. In the oxygenated fractions, 19 components are indicated, the only one identified being methyl nonyl ketone. High correlations have been found between the cohumulone content of the α-acid fraction and the myrcene content of the oil, and between the humulone of the α-acids and the humulene of the oil.

R. E. Essery

3129. **Micro-determination of boron in wines of the Aeolian Islands (Sicily).** G. Bionda and E. Bruno (Ist. di Merceolog., Univ. di Catania, Sicily). *Z. anal. Chem.*, 1957, **155** (3), 183–186.—Microgram quant. of B are estimated photometrically with quinalizarin reagent (20 mg dissolved in 750 ml of conc. H_2SO_4 and 250 ml of glacial acetic acid added). To the sample of wine (0·5 or 0·25 ml) is added 1 ml of saturated $Ca(OH)_2$ soln., and the soln. is evaporated in an oven for 3 hr. at 125°. After the addition of 0·5 ml of conc. H_2SO_4 and 0·12 ml of 30% H_2O_2, the soln. is heated for 3 to 4 hr. at 90°. The residue is shaken with 10 ml of reagent and, after 2 hr., the absorption is measured against that of a blank, a red filter RG2 being used.

J. H. Waton

3130. **Microchemical determination of tartaric acid in wine.** G. Gorbach and W. Vaupotitsch (Inst. f. Biochem. Technol. Lebensmittelchemie und Mikrochemie, Tech. Hochschule, Graz). *Fette, Seif., Anstrichmitt.*, 1956, **58** (10), 865–867.—Tartaric acid is pptd. as K H tartrate, which is then determined iodimetrically. *Procedure*—Pipette a sample of wine (2 ml) into a suitable sedimenting-glass; add about 0·3 g of KCl, acetic acid (40 μl), K acetate soln. (20%) (10 μl) and 96% ethanol (0·4 ml). Stir, with a micro stirring rod, to dissolve the KCl. Wash the rod with a few drops of washing soln. and place the glass in a refrigerator for 2 to 3 hr. Centrifuge and filter the supernatant liquid through a porcelain filter-stick. Wash the ppt. three times with 0·2 ml of washing soln., repeating the centrifuging and filtration. Dissolve the ppt. in 2 to 3 ml of hot water, add $CaCl_2$ soln. (20%) (0·1 ml) and set aside the covered glass to cool. Add sufficient (0·4 g per 10 mg of K H tartrate) of a mixture of KIO_3 (2·14 g) and KI (8·30 g), shake and set aside in the dark for 20 min. Titrate against 0·1 *N* $Na_2S_2O_3$, with 1% starch soln. as indicator. An empirically determined correction for the solubility of K H tartrate is applied.

E. Hayes

3131. **Colorimetric method for the determination of lead in foodstuffs [*e.g.*, wine].** J. Bonastre (Station Agronom. et Oenolog. de Bordeaux, France). *Chim. Anal.*, 1957, **39** (3), 104–105.—The Jaulmes method ("*Analyse des Vins*," 2nd Ed., 1951, Poulain, Montpellier) has been shortened and modified. *Procedure*—The sample of wine (20 ml) and conc. H_2SO_4 (distilled) (2 ml) are placed in a flask and, after distillation of the alcohol, HNO_3 is added dropwise to the boiling liquid at a rate sufficient to oxidise it but avoiding an excess. The residue is neutralised, poured into 20 ml of an aq. soln. of KCN (20 g), citric acid (10 g), conc. aq. NH_3 (500 ml) and water to 1 litre, at pH 9·5, and extracted twice with 10 ml of a $CHCl_3$ soln. of dithizone (30 mg per litre). The Pb is then extracted into an aq. HCl phase and after neutralisation and treatment with ammonium "acetocyanide" soln. (prepared by Jaulmes method), 1 ml of CCl_4 and 2 ml of aq. dithizone soln. are added. After further washes the green colour is compared visually with standards.

E. J. H. Birch

3132. **Application of the chromometric method to the determination of alcohol in vinegars and certain weakly alcoholic food products.** C. Richard (Lab. Hyg. Aliment., Inst. Pasteur, Saigon). *Ann. Falsif.*, 1957, **50**, 8–15.—The vinegar (200 ml) is neutralised with NaOH to powdered phenolphthalein, and 20 ml is distilled off. A suitable aliquot (0·1 to 1·0 ml) is added to a mixture of

10 ml of water and 10 ml of standard $K_2Cr_2O_7$ [0·49% (w/v) in conc. HNO_3]. After 30 min. at room temp., the mixture is treated with 100 ml of KI (1%), and, after a further 2 min., the unreduced dichromate is back-titrated with 0·1 *N* $Na_2S_2O_3$. Suitable aliquots (10 g) of solid foodstuffs are dispersed with 200 ml of water, or suitable volumes of liquids (2 to 200 ml) are similarly diluted, and treated as for vinegar. R. E. ESSERY

3133. **Electrophoretic isolation of dyestuffs in foods.** J. F. Williams (William Arnott Pty. Ltd., George St., Homebush, N.S.W., Australia). *Analyst*, 1957, **82**, 211.—The material (100 g) is extracted for 6 hr. at 45° by stirring slowly with 250 ml of *n*-butanol saturated with 2 *N* HCl. The extract is filtered and the filtrate is concentrated *in vacuo* at a temp. $\not>$ 45°. The dark resinous residue is spread on filter-paper and electrophoresis is carried out at 600 V in the apparatus of Foster (*Brit. Abstr. C*, 1953, 98), with a current of 10 mA and with a pH 12 buffer as electrolyte (100 ml of 0·05 *M* $Na_2B_4O_7$ plus 160 ml of 0·1 *N* NaOH). The component dyes usually separate into discrete zones in 4 to 6 hr. The colour zones are cut out, the dyes are eluted with water and their absorption spectra are recorded. With products containing large amounts of dyestuff, the eluates contain enough material for a paper-chromatographic procedure to be used for identification. The phenol - water - formic acid solvent of Anderson *et al.* (*Anal. Chim. Acta*, 1953, **8**, 530) gave good results in this procedure. A. O. JONES

3134. **Mould prevention in food products. V. Polarographic determination of dehydracetic acid in food products.** Hiroshi Imai and Satoru Oka (Food Ind. Exp. Station, Hiroshima). *J. Agric. Chem. Soc. Japan*, 1956, **30** (12), 747–750.—Dehydracetic acid (3-acetyl-6-methylpyran-2:4-dione) (**I**) gives a reduction wave of a kinetic nature at −1·4 V *vs.* the S.C.E. The $E_{\frac{1}{2}}$ value and the wave height are dependent on the pH and the pressure of the dropping-mercury electrode. The kinetic nature decreases with decrease in pH, but the wave coincides with that of H at pH < 5. The wave height at pH 5·6 is proportional to the concn. of **I** for < 1·0 × 10^{-3} *M*. The sample (*e.g.*, fruit juice, containing < 1 mg of **I** per ml) (50 ml) is extracted with ether, the organic layer is evaporated, and the residue dissolved in *N* NaOH (9 ml). The product is made up to 50 ml with *N* acetic acid (10.0 ml) and water and submitted to polarography. K. SAITO

3135. **Characterisation of higher fatty acids by their hydrazides and certain derivatives of these.** N. P. Buu-Hoï, N. D. Xuong and E. Lescot (Inst. du Radium, Univ., Paris, France). *Bull. Soc. Chim. France*, 1957, (3), 441–443.—Hydrazides of the higher fatty acids are prepared by refluxing the methyl or ethyl esters in ethanol with hydrazine hydrate. Even from unsaturated acids they are solid, recrystallisable from ethanol and melt at ≃ 100°. After a few minutes at 60° with aryl *iso*cyanate or at 75° to 80° with aryl *iso*thiocyanate the hydrazide forms solid recrystallisable 1-acyl-4-aryl-semicarbazides or -thiosemicarbazides, respectively. E. J. H. BIRCH

3136. **Gas-chromatographic analysis of higher fatty acids; up to and including cerotic acid.** R. K. Beerthuis and J. G. Keppler (Unilever Res. Lab., Vlaardingen, Holland). *Nature*, 1957, **179**, 731–732.—The even-numbered saturated fatty acid methyl esters from C_{12} to C_{26} inclusive have been analysed by the use of the gas-density meter of Martin and James (*Biochem. J.*, 1956, **63**, 138) as the detector. The column (113 cm long and 0·4 cm in diameter) was packed with 20 parts of silicone oil "Dow Corning" on Celite 545 screened to particle size 300 to 600 μ and was heated to 257°. The nitrogen flow rate was 24 ml per min. and the analysis took about 1·5 hr. K. A. PROCTOR

3137. **Comparison of low-temperature crystallisation and urea-adduct methods in the analysis of fatty acids of vanaspati.** V. S. Patil and N. G. Magar (Inst. of Science, Bombay). *J. Sci. Ind. Res., B*, 1956, **15** (11), 650–654.—The fatty acid composition of two commercial brands of vanaspati (hydrogenated arachis oil) is determined after fractionation by the two methods. Fractionation of fatty acids and fatty acid esters by the urea-adduct method shows that their tendency to combine with urea decreases with increasing unsaturation, and that combination is favoured by lower temp. The urea-adduct method gives the better separation of unsaturated fatty acids and can be used to supplement the methods for the determination of the component fatty acids of hydrogenated fats. I. JONES

3138. **Quantitative chromatographic determination of the derivatives of vitamin B_6.** P. Fasella and C. Baglioni (Ist. di Chim. Biol., Univ., Rome, Italy). *Acta Vitamin., Milan*, 1956, **10**, 27–29.—Pyridoxine, pyridoxal, pyridoxamine and the phosphates of the last two compounds are separated by paper chromatography when eluted with *n*-propanol - 10% formic acid (4:1). The spots are located in u.v. light, directly or after exposure to NH_3 vapour. The substances are estimated spectrophotometrically after elution with 0·1 *N* HCl. J. H. WATON

3139. **Spectrophotometric determination of small amounts of ascorbic acid in aqueous solutions.** M. L. Tsap (Physicochem. Lab. of the Kiev Sci. Res. Inst. of the Hygiene of Work and Occupational Diseases). *Biokhimiya*, 1956, **21** (5), 534–537.—The sample soln. (1 to 4 ml) is placed in a graduated tube containing 6 ml of a molybdophosphate reagent soln. (prepared by dissolving 1·03 g of ammonium heptamolybdate and 0·047 g of K_2HPO_4 in 100 ml of 1·7 *N* H_2SO_4 and diluting the soln. with the same acid to 250 ml) and then diluted to 10 ml. A control tube contains 6 ml of the reagent soln. diluted to 10 ml with water. Both tubes are stoppered and placed in a boiling-water bath for 10 min., after which they are cooled and the contents are transferred to two cells of a spectrophotometer and the extinction at 825 to 837 mμ is measured. The amount of ascorbic acid is determined from a calibration curve covering the range of 1 to 30 μg of ascorbic acid in 10 ml of water. The method is sensitive to 0·5 μg. G. S. SMITH

See also Abstracts 2915, 3004, 3011, 3062, 3106, 3169.

Sanitation

3140. **Determination of ozone and other oxidants in air.** C. W. Wadelin (Goodyear Tire and Rubber Co., Akron, Ohio, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 441–442.—From 2 to 10^4 parts of O_3 per 10^8 parts of air can be determined by a modification of Ehmert's procedure (*J. Atmos. Terr. Phys.*, 1952, **2**, 189). The O_3 is absorbed in KI (1 g) in 70 ml of

buffer soln. (pH 7) plus 5 ml of 0·001 *N* aq. $Na_2S_2O_3$. The soln. is then acidified with 10 ml of 2 *N* H_2SO_4 and back-titrated with 0·001 *N* KIO_3 soln. to an amperometric end-point. The end-point can be detected with only a calomel electrode, a platinum electrode and a sensitive galvanometer. The standard deviation is 1·45 (parts per 10^8) for O_3 concn. of 15 to 25 (eight samples, triplicate analyses).
W. J. BAKER

3141. **Photometric determination of carbon monoxide in air.** G. Ciuhandu (Inst. für Hygiene, Lab. für Toxikologie, Timişoara, Romania). *Z. anal. Chem.*, 1957, **155** (5), 321–327.—The sample of air is drawn into an inverted, water-filled Erlenmeyer flask by gradually running off the water. If the air contains H_2S, it is first passed through 20% KOH soln. After 1 hr. at 18° to 20°, and the removal of the last traces of water, a reagent consisting of $AgNO_3$ soln. and Na *p*-sulphamylbenzoate in NaOH soln. is introduced. The reduced silver sol after standing overnight is tested photometrically. Extinction coeff. are proportional to the CO contents for the range 0·001 to 0·5% provided that conditions (temp., size of flask) are kept constant. The extinction increases sharply at wavelengths $< 500\ m\mu$; measurements are therefore preferably made at low wavelengths.
W. J. WRIGHT

3142. **Conductimetric estimation of carbon monoxide [in air].** A. Waitman and L. Macoveanu (Inst. of Sci. Res. into the Protection of Workers at the C.C.S.). *Rev. Chim., Bucharest*, 1956, **7** (8), 468–472.—The method is developed from the original work of Kozleava, Petrova and Socolova (LOIT VṬSPS, Leningrad 1949), who converted variation of concn. of gas into variation of current, using the conductivity of a resulting soln. A sample of air is passed through filters to remove moisture, CO_2 and organic solvents, then through a tube containing I_2O_5 heated to 300°. The iodine resulting is removed by absorption in KI soln. The CO_2 in the gas is then absorbed in a dilute soln. of NaOH (free from Na_2CO_3) in a special apparatus described. If the temp. is constant and the soln. of alkali is very dilute (0·0007 *N*), the conductivity will increase with the amount of CO_3^{2-}. By using various mixtures of Na_2CO_3 soln. (0·0007 *N*) with NaOH (0·0007 *N*), a graph can be drawn showing concn. of CO as function of current flowing through the cell.
H. SHER

3143. **Determination of carbon monoxide in air by means of indicator tubes.** L. A. Mokhov and A. V. Demidov. *Lab. Delo*, 1957, **3** (1), 48–50.—The preparation of CO indicator tubes containing $PdSO_4$, stabilised with $(NH_4)_2SO_4$, and $(NH_4)_2MoO_4$ on a silica-gel carrier is described. Air is passed through the tube at a rate of 50 ml per min. for 30 sec., and the colour is compared with a series of standard tints on paper corresponding to the concn. range of 0·005 to 1 mg of CO per litre.
G. S. SMITH

3144. **Determination of carbon tetrachloride in air.** A. A. Belyakov (Gorki State Sci. Res. Inst. of Work Hygiene and Occupational Diseases). *Zavod. Lab.*, 1957, **23** (2), 161–162.—Air at a rate of 15 litres per hr. is passed through two absorption vessels, each containing 3 ml of pyridine or a mixture of equal vol. of acetone and pyridine. One ml of the soln. is placed in a colorimeter tube and mixed with 3 ml of aq. pyridine [28% (v/v)] and 0·1 ml of 0·1 *N* NaOH. The mixture is kept at 85° to 87° for 20 min. The pink soln. after being cooled is treated with 0·4 ml of 80% or glacial acetic acid and 75 to 100 mg (three to four drops) of aniline and diluted to 5 ml with water. After 10 min. a portion of the orange - brown soln. in a 1-cm cell is examined photometrically with a 496-mμ filter. The error in determining 1 μg of CCl_4 in 1 ml of the original soln. is $\simeq 4{\cdot}5\%$. Tetranitromethane interferes but can be removed from the air stream by absorption in Na_2SO_3. Chloroform reacts like CCl_4, but dichloroethane and dichloromethane do not interfere.
G. S. SMITH

3145. **Detection of sulphur dioxide.** P. W. McConnaughey (assignor to Mine Safety Appliances Co.). U.S. Pat. 2,736,638; date appl. 28.2.56.—An elongated tube containing HNO_3-washed and purified silica gel impregnated with iodine soln., which has been mixed with tetramethyldiaminodiphenylmethane (TDD) until the blue colour appears, is useful in the detection of SO_2 in air or other gases, since the blue changes to white in the presence of SO_2. The method is also applicable to the determination of SO_2 when a measured vol. of gas is passed through the tube; the length of the bleached column is a direct measure of the SO_2. It is possible to detect 0·1 p.p.m. by vol. of SO_2 in air.
CHEM. ABSTR.

3146. **Colorimetric determination of aniline [in air] by the diazotisation reaction and the formation of azo compounds.** B. V. Ponomarenko. *Trudy Komiss. Anal. Khim., Akad. Nauk, SSSR*, 1956, **7** (10), 289–294; *Ref. Zhur., Khim.*, 1957, Abstr. No. 1288.—To determine aniline, pass 20 litres of the air through four Petri tubes containing 0·1 *N* HCl, over a period of 15 min. Add to each soln., containing 0·01 to 1·0 mg of aniline, 5 ml of 1·0 *N* HCl and diazotise with four drops of a 10% KNO_2 soln. in the presence of one drop of 5% KBr soln. After stirring for 30 min., neutralise the soln. with 3 ml of 19·3% Na_2CO_3 soln. and mix with two drops of a freshly prepared soln. of 0·5 g of H-acid in 12·5 ml of water. Dilute to 50 ml, and after 30 min. measure the extinction of the crimson colour. Usually it is sufficiently accurate to pass the air through two Petri tubes.
C. D. KOPKIN

3147. **The linear-colorimetric method for the determination of gases and vapours in industrial health investigations.** E. D. Filyanskaya. *Trudy Nauch. Sess. Vses. Nauch. Inst. Okhrany Truda*, 1954 [1955], (1), 198–204; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,347.—The determination of harmful impurities in air is carried out by use of a length of indicator that changes colour on drawing the air through it. Silica gel is used as the reagent carrier. Study is made of the influence in the determination of H_2S of the specific surface of the silica gel and the concn. of a soln. of Pb acetate on the length of the coloured column and its boundary, and the influence of the temp. of drying of the silica gel, of additions and of moisture. It is shown that, on decreasing the specific surface of the silica gel by drying, the length of the coloured column is decreased and the intensity of the colour and the sharpness of the boundary are lowered. The presence of a large amount of reagent on the outer surface of the grains of indicator leads to an intense colour and a sharp boundary. The introduction of Cl^- into the reagents of the indicator powder causes an increase in the length of the coloured

column. The use of indicator tubes for the determination of H_2S, Cl_2, NH_3, petrol vapour, benzene, toluene and nitrogen oxides in air is suggested.
C. D. KOPKIN

3148. **Colorimetric method for determining dissolved oxygen.** C. S. Oulman and E. R. Baumann (Engng Exp. Sta., Iowa State College, Ames, U.S.A.). *Sewage Ind. Wastes*, 1956, **28** (12), 1461–1465.—The use of a spectrophotometer for measuring the colour intensity of the iodine solution obtained in the Winkler test is described.
S.C.I. ABSTR.

3149. **Volumetric determination of calcium and magnesium content [of water] by means of the disodium salt of ethylenediaminetetra-acetic acid.** E. Kint (Soc. Intercomm. des Flandres de Distribution d'Eau, Belgium). *Ind. Chim. Belge*, 1956, **21** (10), 1021–1028.—The use of EDTA (disodium salt), with Eriochrome black T and murexide as indicators, is reviewed. It is proposed that the usual separate aq. NH_3 - NH_4Cl buffer and stabilised Eriochrome black T indicator should be replaced by a combined buffer - indicator mixture, consisting of 80 g of Na_2CO_3 dissolved in 750 ml of water, 0·5 g of Eriochrome black T, 4·5 g of hydroxylamine hydrochloride in 150 ml of water and 0·616 g of $MgSO_4.7H_2O$ plus 0·93 g of the EDTA (disodium salt). The solution is made up to 1 litre and 1 ml is used for each 50 ml of water to be titrated. This method is compared with others and interferences are discussed. E. J. H. BIRCH

3150. **Modified method for the determination of copper in boiler feed water.** D. Parkhouse (Div. Lab., Croydon "B" Power Station, England). *Chem. & Ind.*, 1957, (8), 224–225.—In this method a complete extraction of the coloured copper complex formed with Na diethyldithiocarbamate (**I**), is not made, but calibration is based on standard partition coeff. between fixed vol. of water and CCl_4. The sample (500 ml) should be collected in a 1-litre separating funnel containing 0·5 ml of conc. HNO_3 to prevent deposition of Cu on the walls of the flask, and a standard soln. of Cu, 5 ml of aq. NH_3 - ammonium citrate buffer soln., 5 ml of **I** soln., and 10 ml of CCl_4 are added. After 5 min. agitation, the CCl_4 layer is allowed to separate, run into a test-tube cell, and centrifuged for 1 min. Its absorption is measured with violet filter 601.
W. J. WRIGHT

3151. **Determination of thorium in mineral spring water and silicate minerals with thoron.** Tomitaro Ishimori, Kaoru Ueno and Hirohisa Amatatsu (Fac. Sci., Kyushu Univ., Hakozaki, Fukuoka). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1705–1707.—The photometric determination of Th with thoron [1-(*o*-arsonophenylazo)-2-naphthol-3:6-disulphonic acid] (**I**) was applied to the determination of Th separated from interfering ions such as Fe, Zr, Ti, U or La with the ion-exchange resin Amberlite IR-120. The small loss of Th during the separation was corrected by the use of carrier-free ^{234}Th. The sample soln. (1 to 100 μg of Th) is mixed with a known amount (*a* counts per min.) of ^{234}Th (Dyrssen, *Svensk Kem. Tidskr.*, 1950, **62**, 153) and made 2 *N* with HCl soln. This soln. is passed through a column of IR-120, washed with 2 *N* HCl and water and eluted with 0·5 *M* oxalic acid. The eluate is heated, to remove oxalic acid by sublimation, then evaporated to dryness with $HClO_4$ and HNO_3, and the activity is measured (*b* counts per min.). The residue is dissolved in conc. HCl (four drops), water (80 ml) and hydroxylamine hydrochloride (10%, 1·0 ml), heated for $\simeq$ 10 min., then cooled and treated with freshly prepared 0·1% **I** soln. (1·0 ml) and the extinction measured at 545 mμ (*c* μg of Th). The amount of Th is calculated as ac/b μg. A large amount of Fe is removed with an anion-exchange resin in 10 to 12 *N* HCl, as are Zr and Ti.
K. SAITO

3152. **Measurement of low-level radioactivity in water.** L. R. Setter and A. S. Goldin (Robert A. Taft San. Engng Center, USPHS, Cincinnati, Ohio). *J. Amer. Wat. Wks Ass.*, 1956, **48**, 1373–1379.—The sample is placed in a small dish inside a counter chamber which detects α-radiations and β-radiations except those of extremely low energy. The α-activity is counted, without interference from β-radiations, by adjusting the voltage to an appropriate level. Combined α- and β-activity is then counted at a voltage suitable for β-activity. The method is sensitive to 10 to 30% of max. permissible concn. for unknown isotopes. S.C.I. ABSTR.

3153. **Determination of radon in thermal springs.** B. Čerček. *Rep. J. Stefan Inst., Ljubljana*, 1956, **3**, 79–85 (in English).—A radiometric method and apparatus for quant. assay of radon in liquids are described. Electric pulses produced by alpha-disintegrations in the ionisation chamber are electronically amplified and counted. The lower limit of detection is about 10^{-11} curie of radioactivity. The apparatus may be used for quant. assaying of radium samples in soln. by the emanation technique. O. M. WHITTON

3154. **Separation and concentration of underground water by the use of an anion exchanger.** Yoshihiko Mizutani (Earth Sci. Inst., Fac. of Sci., Nagoya Univ., Chigusa-ku, Nagoya). *Japan Analyst*, 1956, **5** (11), 620–622.—Sulphate (< 100 mg per litre) in underground water can be rapidly concentrated (< 3 hr.) by the use of the weakly basic anion-exchange resin Amberlite IR-143(Cl). The sample soln. (500 ml) is made acid with 6*N* HCl (1 to 2 ml) and passed through (5 ml per min.) a column of the resin, which is washed with 0·1 *N* HCl (20 ml) to remove the remaining metal and PO_4^{3-}, and the SO_4^{2-} are eluted with 0·5 *N* aq. NH_3 soln. (30 ml., 1 ml per min.). The eluate is made acid to methyl red, treated with 10% $BaCl_2$ soln. and determined gravimetrically. Only NH_4^+, SO_4^{2-}, Cl^- and NO_3^- are found in the eluate.
K. SAITO

3155. **Colorimetric determination of aluminium in industrial waters containing iron.** Katsumi Goto (Fac. Engng, Hokkaido Univ., Sapporo, Japan). *Chem. & Ind.*, 1957, (11), 329.—The method described by Gentry and Sherrington (*Analyst*, 1946, **71**, 432) is adapted to water analysis, Fe being masked by the addition of *o*-phenanthroline. *Procedure*—Add HCl (1:10) (0·5 ml) and hydroxylamine hydrochloride soln. (10%) (1 ml) to the sample (30 ml containing < 4 p.p.m. of Al) and heat gently. Cool and add *o*-phenanthroline soln. (0·12%) (3 ml) and Na acetate [a 40% (w/v) soln. of the hydrate] (0·5 ml). Then add 8-hydroxyquinoline soln. (3 ml) [dissolve 2 g in glacial acetic acid (5 ml) and dilute to 200 ml with water] and Na acetate soln. (2 ml). Extract with $CHCl_3$ (10 ml), wash the extract with water and dry over Na_2SO_4. Measure the absorption at 400 to 420 mμ. Several ions interfere. G. S. ROBERTS

3156. **Recommended methods for the analysis of trade effluents. Methods for the determination of hardness, calcium and magnesium.** The Joint A.B.C.M. - S.A.C. Committee on Methods for the Analysis of Trade Effluents. *Analyst*, 1957, **82**, 197–200.—To determine total hardness, the total cations are determined by ion exchange followed by determination of the alkali-metal cations. The difference, expressed as $CaCO_3$, is the total hardness. By another method the amount of standard mixed alkali required to precipitate the "non-alkali" cations is determined. Temporary hardness is determined by titration with 0·1 *N* HCl. To determine Ca, the ignited residue after evaporation is dissolved in HCl, the soln. is boiled with Na_2SO_4, filtered to remove $PbSO_4$, and an aliquot of the filtrate is adjusted to a definite slight alkalinity and after addition of KCN and murexide indicator is titrated with EDTA (disodium salt) soln. To determine Mg, another aliquot of the filtrate is neutralised with aq. NH_3, then KCN and a buffer soln. are added and the liquid is titrated with EDTA (disodium salt) soln., with Solochrome black WDFA as indicator. The titre is calculated to Ca, the Ca found in the first titration is deducted, and the remainder is calculated to Mg. A. O. Jones

See also Abstracts 2941, 2944, 2973, 3024, 3189.

Agriculture and Plant Biochemistry

3157. **The application of spectrochemical methods to agricultural problems.** R. L. Mitchell and R. O. Scott (Macaulay Inst. for Soil Res., Aberdeen, Scotland). *Appl. Spectroscopy*, 1957, **11** (1), 6–12.—Analyses originating from diverse types of materials have been examined by a standard procedure in which biologically important trace metals are concentrated into an alumina matrix (*cf. Spectrochim. Acta*, 1948, **3**, 367). Alkali and alkaline-earth metals, phosphates and other anions, together with Mn, all of which might cause spectrographic difficulties in certain types of plant materials, are thus rejected. The powder is mixed with an equal quantity of carbon, for steady burning, and the arc excitation is carried out in a cathode-layer type carbon electrode of about 10 mg capacity packed by hand. A 10-mm gap is used with an arc current of 9 amp. Working curves, obtained from standard mixtures in a matrix of Al_2O_3 and Fe_2O_3, have been derived for Co, Ni, Mo, Sn, Pb, Zn, Ti, V, Cr, Ga, Ge, Be, Ag and Au, the sensitivity ranging from 0·015 μg of Ag in the electrode (*i.e.*, 0·01 p.p.m. in the sample) to 3 μg of Zn in the electrode (2 p.p.m.). Direct arc analyses of Cu and Mn in plant ash have been determined by the method of Farmer (*cf. Spectrochim. Acta*, 1950, **4**, 224), a boring 4 mm deep and 2·4 mm wide in a carbon electrode 3·85 mm outside diam. being filled and arced as above. Duplicate readings are necessary. Porous cup solution spark excitation methods of determination for 36 elements are discussed. The tabulated sensitivities show that Be, Cu, Mg and Mn are detectable at levels $< 0{\cdot}1$ p.p.m. using the Hilger quartz spectrometers. Alkali and alkaline-earth elements determined by Lundegardh flame technique or a three-channel flame photometer are mentioned. E. G. Cummins

3158. **Flame-photometric estimation of copper. Application to plant tissue.** H. F. Massey (The Univ., Lexington, Ky, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 365–366.—Copper (concn. $\gtrsim$ 200 μg) in the liquid from the acid digestion of $\simeq$ 5 g of plant tissue can be determined quickly by extraction from a 200-ml aliquot (adjusted to 0·1 *N* HCl) with a 0·5% (w/v) soln. of dithizone in $CHCl_3$ - liquid paraffin (1 + 1), followed by direct flame photometry of the organic extract. A blank is run and the concn. of Cu is calculated from a standard curve. The mean deviation (four analyses) is $\simeq$ 2%, and the results agree with those obtained by the spectrophotometric method used in agricultural laboratories. W. J. Baker

3159. **Analytical studies on fluoride. II. Colorimetric determination of fluoride in plants with thorium and "Neo-thorin."** Koichi Emi and Tadashi Hayashi (Fac. of Sci., Okayama Univ., Tsushima, Okayama). *J. Chem. Soc. Japan, Pure Chem. Sect.*, 1956, **77** (11), 1656–1658.—The prep. of the sample for the colorimetric determination of F^- with the complex of Th and Neo-thorin [*o*-(1:8-dihydroxy-3:6-disulpho-2-naphthylazo)benzene-arsonic acid] (**I**) (*Anal. Abstr.*, 1956, **3**, 2475) was studied with tea leaves. The sample (10 g) is mixed with CaO (0·3 g) and a small amount of water; the mixture is evaporated and the residue heated at $\simeq$ 250° and then at 650° for 30 min. There is no appreciable loss of F provided that the temp. is kept below 750°. The ash is distilled with dil. H_2SO_4 soln. and the reduction in the extinction of **I**, after adding the distillate, is measured. K. Saito

3160. **Comparative study of methods for the determination of the isotopes ^{32}P, ^{45}Ca and ^{35}S in plant tissues.** R. de Loose (Inst. Agronomique, Ghent). *Chim. et Ind.*, 1956, **76** (6), 1291–1298.—Various methods described in the literature are summarised and their reproducibility is discussed. The mean standard deviations are: 2·07% for ^{32}P, by a modification of the method of McKenzie and Dean (*Anal. Chem.*, 1948, **20**, 559, and 1950, **22**, 489); 1·82% for ^{45}Ca, by a modification of the method of Norris and Lawrence (*Anal. Chem.*, 1953, **25**, 956); and 1·93% for ^{35}S by pptn. as $BaSO_4$, followed by homogeneous distribution of the ppt. on aluminium plates, a method based on that employed for the determination of ^{14}C by Govaerts (*Bol. Radioactividad*, 1953, **25**, 104). J. M. Jacobs

3161. **Rapid method for determination of malic acid.** A. E. Goodban and J. B. Stark (U.S. Dept. of Agric., Albany, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (2), 283–287.—Cationic material is removed from the sample on a short column of cation-exchange resin. The acids, including malic, are then adsorbed on an anion exchanger. An initial elution of this column removes weakly held acids, which interfere with the colorimetric procedure; the malic acid is then removed by increasing the concn. of the eluting soln. An aliquot of the eluate containing the malic acid is heated with 2:7-dihydroxynaphthalene and H_2SO_4 and the resulting colour is measured at 390 mμ. The mean recovery from eight determinations of a standard malic acid soln. was 100·3% and the coeff. of variation was $\pm$ 2·2% at the 15-mg level. The method was applied to aq. plant extracts. G. P. Cook

3162. **A chromatographic analysis of the free amino acids, organic acids and sugars in flax *Linum usitatissimum*.** I. A. M. Cruickshank (D.S.I.R., Low Temp. Res. Station, Cambridge). *J. Sci. Food Agric.*, 1957, **8** (1), 26–30.—A chromatographic method for the qualitative analysis of the

amino acids, organic acids and sugars present in flax tissues is described. Twenty-three compounds associated with the normal metabolism of flax tissues are identified. H. B. HEATH

3163. **Micro-method of determining coumarin in vegetable material.** K. Blyaim (Biochem. Lab., Inst. for the Selection and Acclimatisation of Plants, Pulavy, Poland). *Biokhimiya*, 1956, **21** (6), 689–693.—The sample (20 mg) of dried and finely divided material is extracted with 50 ml of $CHCl_3$, the soln. is made up to 50 ml and a 10-ml aliquot is passed through a chromatographic column (Relovets earth) followed by pure $CHCl_3$. The soln. is evaporated *in vacuo* to $\simeq$ 5 ml, 5 ml of methanol is added and the $CHCl_3$ is evaporated off completely. After addition of 5 ml of a 5 *N* soln. of KOH in methanol, the soln. is made up to 25 ml with methanol, the fluorescence is measured, and the content of coumarin is calculated from a calibration curve. The standard deviation of 12 results having a mean of 1·58% is $\pm$0·079. G. S. SMITH

3164. **The fluorimetric determination of total, free and ester flavin in plant tissues with a micro-fluorimeter.** Hiroshi Kondo (Fac. of Agric., Meijo Univ., Nakamura-ku, Nagoya). *J. Agric. Chem. Soc. Japan*, 1956, **30** (11), 690–695.—The fluorimetric determination of a micro amount ($<$ 10 μg in 1 g of the tissue) of total (**I**), free (**II**) and ester flavin (**III**) as well as flavin-adenine dinucleotide and mononucleotide was studied with reference to the removal of interfering substances. Trichloroacetic acid (**IV**) is the best precipitant for proteins. The sample is extracted with warm water (80°, $>$ 40 times the weight of the sample) and centrifuged; the supernatant liquid is treated with **IV** (20%, 1 ml), decomposed photochemically, and extracted with $CHCl_3$, and the fluorescence of **I** is measured. For the separate determination of **II** and **III**, the aq. extract is divided into five portions, each of which is extracted with water, with or without being treated with benzyl alcohol or being submitted to photolysis (Bessy *et al.*, *J. Biol. Chem.*, 1949, **180**, 755). The amounts of **II**, **III** and the nucleotides are calculated from an empirical formula. K. SAITO

3165. **Use of thiourea for the colorimetric determination of phosphoric acid [in soil].** A. M. Meshcheryakov. *Pochvovedenie*, 1956, (3), 88–90; *Ref. Zhur., Khim.*, 1956, Abstr. No. 78,481.—(*i*) Neutralise the soln. containing 0·01 to 0·06 mg of P_2O_5 with H_2SO_4, HCl or NaOH in the presence of three or four drops of a satd. soln. of 2:4-dinitrophenol. Add 2 ml of molybdate reagent (**I**) (3·762 g of MoO_3 is dissolved by boiling with 75 ml of H_2SO_4, sp.gr. 1·785, the soln. is cooled and poured in a thin stream into 300 ml of water and, after cooling, made up to 500 ml) and 2 ml of a 5% soln. of thiourea (**II**), and dilute to 40 or 45 ml. The soln. is shaken after each addition. Standard soln. are prepared in the same way from potassium phosphate. Keep the soln. at 80° to 90° for 30 min., cool to between 18° and 20°, dilute to 50 ml and read on the colorimeter. If a cloudiness or ppt. appears, filter through a 0·5-ml asbestos funnel or set aside for 24 hr. Substances from humus interfere, and are oxidised by adding to the original soln. (20 to 40-ml extract from the soil with 1% ammonium or potassium carbonate soln.) 3 to 5 ml of 10% H_2SO_4, boiling, adding 2 to 4 ml of 0·1 *N* $KMnO_4$ and boiling for 2 min. Then proceed as above. (*ii*) After neutralising the soln., add 2 ml of **I**, 2 ml of **II**, and dilute to 40 or 45 ml. To the sample and standard soln. add 0·5 ml each of freshly prepared $SnCl_2$ soln. (70 mg of tin shavings is dissolved in 2 ml of HCl, sp.gr. 1·19, then a further 2 ml of this acid is added, and diluted to 25 ml), mix, dilute to 50 ml, mix and after 1 min. read on the colorimeter. In the presence of substances from humus, oxidise as described above. C. D. KOPKIN

3166. **Evaluation of the chemical fertility of soil. II. Estimation of total phosphorus of the soil.** C. Ferrari (Ist. di Chim. Agr., Univ., Bologna, Italy). *Ann. Sper. Agr.*, 1956, **10**, 813–817.—Total P in soil is determined colorimetrically by the formation of the blue reduced molybdophosphoric acid. Careful control of the pH avoids interference from any Si not rendered insol. during the attack on the sample. Arsenic does not interfere if it is reduced to As^{III}. *Procedure*—A 1-g sample of finely divided soil is heated for 15 to 20 min. with 12·5 ml of conc. H_2SO_4 in a Kjeldahl flask until particles of C are dissolved. Potassium perchlorate (0·1 to 0·2 g) is added, and the mixture is boiled for 10 to 15 min., with frequent shaking. After being cooled and diluted, the soln. is made up to 250 ml, and a 25-ml sample is filtered off. (It is desirable to titrate a 5-ml portion with *N* NaOH so that the acidity can be adjusted to $\leqslant$ 7 ml of *N* H_2SO_4.) After dilution, 5 ml of ammonium molybdate soln. (1·44%), 2 ml of aq. ascorbic acid (2·5%) (or 1 ml of 1% hydrazine sulphate soln.) are added, and the soln. is kept on a water bath for 30 min. The cooled soln. is made up to 100 ml, and the extinction measured. J. H. WATON

3167. **Quantitative infra-red analyses of mixtures of isomeric or closely related substances. Mixtures of chlorinated insecticides.** I. R. C. McDonald and C. C. Watson (D.S.I.R., Wellington, New Zealand). *Anal. Chem.*, 1957, **29** (3), 339–346.—Inactive and active isomers in pesticides have been estimated in the presence of one another by the differential double-beam i.r. spectrometric technique described. Special emphasis is laid on the instrument-setting conditions for quantitative analyses, and the results of setting changes and various test performances are tabulated. Any solvent-soluble organic mixture may be analysed on a double-beam spectrometer with a 1-mm fixed-thickness cell and a variable path length cell by this method, given pure samples of the substances sought, and the desired substance may be determined to an accuracy within 2% of the amount present. E. G. CUMMINS

See also Abstracts 2915, 3069.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

3168. **An auxiliary device for the micro-Kjeldahl nitrogen determination.** K. Eder (Ecole de Chimie, Univ. Geneva, Switzerland). *Mikrochim. Acta*, 1957, (2), 227–229.—A neat and safe procedure is described for the transfer of the sample substance after decomposition with H_2SO_4 to the Kjeldahl distillation flask. Items of simply constructed apparatus for carrying out the operations are described and illustrated. D. F. PHILLIPS

3169. **Graphical representation of weight changes in thin layers by means of a filmograph.** H. P. Kaufmann (Dtsch. Inst. f. Fettforschung, Münster/Westf., Germany). *Fette, Seif., Anstrichmitt.*, 1956, **58** (10), 844–847.—An electronic micro-balance is modified to take four thin plates (12·5 sq. cm) on the end of the quartz weighing arm. The balance can be used to study the effect of gases on thin layers of materials spread on the plates. Examples of its use include studies on the loss of water from margarine, soaps and cosmetics, and on the oxidation of drying oils. E. HAYES

3170. **A dispenser and reservoir for concentrated sulphuric acid.** T. G. Morris (M.R.C. Pneumoconiosis Res. Unit, Llandough Hosp., Penarth, Glam.). *Lab. Practice*, 1957, **6** (4), 223.—An apparatus is illustrated and described which is suitable for storing and dispensing with accuracy small (0 to 10 ml) volumes of conc. H_2SO_4. During the storage the acid is protected from moisture and is never exposed to pressure or vacuum. M. F. C. LADD

3171. **Filling device for simple micro-burettes.** K. Eder (Ecole de Chimie, Univ. Geneva, Switzerland). *Mikrochim. Acta*, 1957, (2), 226–227.—A simple device is described and illustrated for filling an ordinary micro-burette through its tip by means of air pressure applied by means of a blow ball. The advantages of simple micro-burettes used in conjunction with the device for occasional titrations as compared with the more expensive automatic-filling burettes are emphasised. D. F. PHILLIPS

3172. **Burette arrangement for some special titrations.** W. J. Kirsten (Pharmacia Res. Lab., Uppsala, Sweden). *Anal. Chem.*, 1957, **29** (3), 460–461.—The burette illustrated can easily be operated by inert-gas pressure and the solvent does not pass through the control tap. The design is for reagents of the Karl Fischer and titanous trichloride types. Several modifications of the Teflon Ultramax stopcock are described. E. G. CUMMINS

3173. **Titration flask.** I. Kukin (Gulf Res. and Dev. Co., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 461.—To assist the detection of visual colorimetric end-points, particularly with dark solutions, this flask has been designed with an elongated neck and side-arm, both of small diameter (19 mm outside). Magnetic stirring of the sample solution is an important feature. E. G. CUMMINS

3174. **Apparatus for anaerobic determination of the pH of blood at 38° C.** P. Astrup and S. Schrøder (Rigshospitalet, Copenhagen). *Scand. J. Clin. Lab. Invest.*, 1956, **8** (1), 30–32.—A combined glass-calomel electrode that makes contact through a porous disc is fitted into a small water-jacketed chamber kept at 38°. The chamber is connected at the bottom through tubing with a movable mercury reservoir, and at the top through a narrow channel with a receiving cup. A rubber connection from the syringe in which the blood has been collected is pushed into the narrow channel of the receiving cup and the blood is drawn into the chamber without air being admitted. The reproducibility is within 0·001 pH unit. E. KAWERAU

3175. **New low-hold-up high-efficiency laboratory distillation column.** J. D. Ray (Dept. of Chem., Stanford Univ., Stanford, Calif., U.S.A.). *Rev. Sci. Instrum.*, 1957, **28** (3), 200–201.—A Vigreaux-type column has been modified so that the indentations are perpendicular to the walls and spaced so that no surface is more than 1·8 mm from another. The formation of hanging drops and flooding is very much reduced. G. BURGER

3176. **A separator for removing heavy minerals from flour and other foodstuffs.** A. W. Hartley (Spillers Central Lab., Station Road, Cambridge, England). *Analyst*, 1957, **82**, 214–215.—The separator described and illustrated is a smoothly tapering conical separator with an A10 ground joint at the bottom end, over which fits a short tube having an A10 neck and attached to the separator by lugs and springs. Inside the throat of the separator a ground seating is made to take a glass rod which acts as a stopper, so that the small tube can be removed at any stage of the sedimentation. With this apparatus a 90% recovery can be attained of inorganic materials such as reduced iron, aerating agents, chalk B.P., some powder improvers and metallic fragments. A. O. JONES

3177. **A special drying oven for drying and developing paper chromatograms.** P. Neuenschwander and R. J. Peltonen (Forschungslab. Staatlichen Alkoholmonopols, Helsinki). *Mikrochim. Acta*, 1957, (1), 71–79.—The requirements of a drying oven used for drying and developing paper chromatograms are discussed. Detailed designs and instructions for the construction of such an oven and the practical experiences gained during its use are given. P. S. STROSS

3178. **Simple automatic apparatus for spotting large volumes of liquid on chromatogram papers.** W. G. Duncombe and B. W. E. Peaple (Nat. Inst. for Res. in Dairying, Univ. of Reading, England). *Analyst*, 1957, **82**, 212–214.—By means of the apparatus described and illustrated a vol. of up to 0·5 ml of solute can be applied to chromatographic paper as a single spot. The apparatus, once started, requires no attention and is automatically switched off when the pre-determined vol. has been delivered. It consists of an Agla micrometer syringe driven by a low-speed synchronous motor. A Perspex disc is attached to the moving part of the micrometer in such a way as to make contact with a micro switch when the zero mark is reached. A. O. JONES

3179. **Modified end-window counting tube for paper chromatograms.** R. C. Fuller (Brookhaven National Lab., Upton, New York, U.S.A.). *Science*, 1956, **124**, 1253.—A modified "Scott tube" for counting radioactive compounds after autoradiography is described. H. F. W. KIRKPATRICK

3180. **Device for concentrating and eluting the spots from chromatograms.** W. S. Reith (Hammersmith Hospital, London). *Nature*, 1957, **179**, 580–581.—In the device described and illustrated, ten similar spots or zones are placed, in two groups of five, on opposite sides of Whatman No. 20 paper, the bundle being enclosed between two Perspex plates held together by rubber bands. A strip of Whatman 3 MM paper conducts the solvent to this assembly; the plates are enclosed in a Cellophane envelope. The ascending solvent elutes and concentrates the compounds into the tip of the

No. 20 paper; after ≃ 12 to 20 hr. the assembly is inverted and the compound is eluted from the tip by the smallest possible vol. of the descending eluent dripping slowly from the paper. The procedure is useful when many chromatograms containing small amounts of compound (especially of low solubility) must be eluted simultaneously.
W. J. BAKER

3181. **Simple pressure regulator for micro-analysis of carbon and hydrogen.** K. Eder (Ecole de Chimie, Univ. Geneva, Switzerland). *Mikrochim. Acta*, 1957, (2), 224–225.—Pressure regulation is obtained by attachment of a glass side-arm (approx. 2 cm diam. × 14 cm long) to the fixed vessel. The setting is made through addition or withdrawal of water by means of a pipette. The same effect is obtained by furnishing the side-arm with a bung drilled to accommodate a withdrawable plunger (small test-tube). Improved control is obtained by means of arbitrary graduations on the fixed vessel. A simple arrangement of glass taps is suggested whereby it is possible to operate with only one pressure regulator when using cylinder oxygen and air from a gas-holder.
D. F. PHILLIPS

See also Abstracts 2958, 3071.

Optical

3182. **A new atomiser for the flame photometer.** H. Straubel (Physik. Inst., Univ. Jena, Germany). *Dechema-Monogr.*, 1956, **27**, 74–80.—The atomiser operates on an electrostatic principle and is more efficient than the conventional types which use compressed air (*cf. Anal. Abstr.*, 1955, **2**, 3259).
A. R. ROGERS

3183. **Pneumatic atomiser for flame photometry.** I. Perman. *Rep. J. Stefan Inst., Ljubljana*, 1956, **3**, 179–187 (in English).—The pneumatic atomiser with spray chamber described and illustrated is simple, sturdy, easily dismantled and cleaned, and resistant to corrosion and erosion. The effect of various conditions on spraying was studied. A reading can be made with < 0·05 ml.
O. M. WHITTON

3184. **New applications of addition-standard technique in flame spectrophotometry.** Shouzow Fukushima, Kizashi Takahashi, Satoshi Terasaka and Kiyoteru Otozai (Univ. Osaka, Japan). *Mikrochim. Acta*, 1957, (2), 183–195 (in English).—Two methods are described which are designed to avoid errors caused by a multiplicative interference of the concomitant elements present with emission intensities in flame photometry. Principles of the proposed methods, known respectively as the "concentration-coefficient" and "intensity-coefficient" techniques, are described, together with demonstrating experiments in which the Beckman DU flame spectrophotometer is used with an acetylene - oxygen burner. The concentration-coefficient method was applied to six samples containing 0·87 to 5·2 milli-equiv. of NaCl per litre as specified substance and 5% of sucrose as an interfering concomitant. The average error was 1·8% of the concn. sought. The intensity-coefficient method was applied to seven samples containing 0·87 to 3·5 milli-equiv. of NaCl per litre as specified substance and 0·5% of KCl as an interfering concomitant. The average error was 2·0 to 2·8%. Possible modifications of the methods are suggested in order to extend the application of these techniques. (See also *Anal. Abstr.*, 1957, **4**, 2448.)
D. F. PHILLIPS

3185. **Improvements in or relating to spectroscopes.** R. Graesser, Ltd. (Inventors: F. Singleton and G. L. Collier). Brit. Pat. 760,729; date appl. 16.12.53.—The resolution achieved by direct i.r. spectroscopy may be greatly improved by artificial means so that overlapping bands are separated. The resulting separated bands are then employed to determine the quant. composition of complex mixtures, particularly of org. substances such as phenols, by the measurement of an even (preferably the second) derivative of the logarithm of the light intensity or percentage transmission. The method of testing for the presence of a particular component in a mixture comprises measuring the light absorption or percentage transmission of the mixture over a range including a wavelength at which this component exhibits an absorption max., and twice differentiating this observed length with respect to wavelength and measuring the value of the second derivative which will show a max. at the same wavelength as the known absorption max. The quant. determination of the amount of component present is achieved by first taking the logarithm of the light absorption or percentage transmission and subsequently differentiating twice. The amplitude of the resolved peaks will then indicate directly the quantity of the component present when compared with the amplitudes of the absorption maxima in the corresponding curve obtained from a known sample of the component. The apparatus comprises a spectroscope having an optical system adapted to resolve radiation of the wavelength range within which the measurements are to be made, a cell for the material being tested, means for scanning the spectrum produced by the optical system at a given rate, and means for producing an electrical signal proportional to the intensity of the portion of the spectrum that is scanned. It also includes at least two differential circuits in sequence between the signal producing means and means for recording, determining or displaying the value of a final output signal. When a quant. determination is to be made, a logarithmic circuit, to which the signal is applied as an input, is interposed between the signal source and the first differential circuit.
J. M. JACOBS

3186. **An examination of the Unicam S.P. 600 spectrophotometer.** D. R. Curry and P. H. Scholes [Metallurgy (General) Divisional Lab., The British Iron and Steel Research Ass., Sheffield]. *Metallurgia, Manchr*, 1956, **54**, 145–149.—Results of practical tests, in which the instrument was used as an absorptiometer and a spectrophotometer, are reported.
W. J. WRIGHT

3187. **Console comparator microphotometer featuring high screen intensity and a null-ratio measurement system.** H. B. Beal, R. K. Brehm and R. F. Jarrell (Jarrell-Ash Co., Newtonville, Mass., U.S.A.). *J. Opt. Soc. Amer.*, 1957, **47** (4), 306–311.—The microphotometer described has been designed primarily for the measurement of line densities on emission spectrograms, although it may be applied to the assessment of X-ray diffraction patterns, radiographs and small areas of photographic records such as electron micrographs. An enlarged image (× 15) of the negative being measured is displayed on a viewing screen at the centre of the console; a comparison spectrogram or

masterplate may also be projected in juxtaposition on this screen. A fiducial mark on the screen indicates which spectral line is being measured. Photomultipliers are used in the null-ratio measuring circuit, which is of sufficient sensitivity to measure emulsion areas as small as 200 μ^2, with electronic stability of $\pm$ 0·25% of full-scale deflection. The instrument can be readily adapted for use with a recorder. B. S. COOPER

3188. **The adaptation of a commercial double-beam infra-red spectrophotometer for use with a grating.** H. C. Mattraw and F. P. Landis (General Electric Co., Schenectady, N.Y., U.S.A.). *Appl. Spectroscopy*, 1957, **11** (1), 31–38.—The installation of a 60 line per mm Bausch and Lomb grating in place of the prism in the Baird double-beam spectrophotometer is described. Details of the drive linkage are given. The solutions to the problem of overlapping orders are tested, and illustrations show the resolution of the instrument in various orders. E. G. CUMMINS

3189. **Thermostated microcell adapter for Perkin-Elmer infra-red spectrophotometers.** S. T. Zenchelsky and J. S. Showell (Ralph G. Wright Lab., Rutgers Univ., New Brunswick, N.J., U.S.A.). *Anal. Chem.*, 1957, **29** (1), 167–169.—The i.r. spectrophotometric technique of Trenner *et al.* (*cf. Appl. Spectroscopy*, 1953, **7**, 166) for the determination of the deuterium content of water demands thermostatic control of the water. A thermostatically controlled microcell adapter is described which is suitable for use with the standard microcell. It slides easily into the externally located cell mount of the instrument and may be easily removed when not in use. It may be operated from any standard laboratory circulating bath, and its construction is simple and inexpensive. L. S. ADLER

3190. **Effects of grinding during the preparation of alkali halide discs on the infra-red spectra of hydroxylic compounds.** V. C. Farmer (Macaulay Inst. for Soil Research, Craigiebuckler, Aberdeen, Scotland). *Spectrochim. Acta*, 1957, **8** (6), 374–389.—Changes in the spectra of phenols and organic acids induced by grinding with alkali halides are ascribed to the adsorption of molecules on the surface of the alkali halides through their hydroxyl groups. Spectra illustrated show the differing behaviour of various alkali halides, and the importance of the duration of grinding time is considered. Work with benzoic, phenylbutyric, cinnamic and crotonic acids and various phenols is included. Optimum grinding times are discussed and KBr is selected as the best material. E. G. CUMMINS

3191. **Application of vapour chromatography to infra-red spectroscopy of liquids.** H. E. Bellis and E. J. Slowinski, jun. (Univ. of Connecticut, Storrs, U.S.A.). *J. Chem. Phys.*, 1956, **25**, 794.—By minor modifications of the authors' vapour fractometer, chromatographically pure organic liquids can be prepared from an initial sample volume of 0·03 ml. The flow-meter, where mixing might occur, is bypassed by connecting the detector cell to a small Pyrex-glass trap with a short length of heated Monel metal tubing. *Procedure*—Ascertain by trial the times at which the various components of the sample being fractionated arrive at the trap, then insert the trap into the gas stream at the appropriate time. This ensures almost complete recovery of the desired pure component. Remove the trap from the system and flame-seal its entrance and exit tubes. Condense the sample at the foot of the small tube (4 mm diam.) by gently heating the upper portion of the trap. Break the cell from the trap and draw the sample into a medicine dropper having a capillary tip. Assemble absorption cells from two circular (25 cm × 5 mm) sodium chloride blanks and an amalgamated demountable cell spacer of 0·002 in. thickness in the usual way. Drill two small holes obliquely into one of the blanks to allow for the introduction of approx. 0·015 ml of sample from the medicine dropper. Seal the cell with Teflon plugs. An infra-red spectrum was obtained on 0·03 ml of *cyclo*octane of 97·5% purity. No impurity was observed on re-running the remainder of the sample through the fractometer. D. F. PHILLIPS

3192. **New instruments for the continuous analysis of gases with the aid of infra-red radiation.** K. H. Winterling (Hartmann & Braun A.-G., Frankfurt a. Main). *Dechema-Monogr.*, 1956, **27**, 286–298.—A review. A. R. ROGERS

3193. **An atomic-absorption spectrophotometer and its application to the analysis of solutions.** B. J. Russell, J. P. Shelton and A. Walsh (C.S.I.R.O., Melbourne, Australia). *Spectrochim. Acta*, 1957, **8** (6), 317–328.—The spectrophotometer described has been constructed mainly from readily available components. The sample is sprayed into a flame and the absorption by the flame of an atomic resonance line of the element to be estimated is measured, the apparatus being so arranged that the absorption measurement is independent of any radiation emitted by the flame. The results confirm that, in contrast to the emission method, the sensitivity of the absorption method is independent of the excitation potential of the spectral line used. Estimated limits of detection for Na, K, Cu, Zn, Cd, Au, Ag, Rb, Cs, Te, Mg, Fe, Cr and Ni are tabulated, ranging from 0·1 p.p.m. for Na, Zn, Cd and Mg to 40 p.p.m. for Fe and Cr. E. G. CUMMINS

3194. **Quinine calibration of the Aminco-Bowman spectrophotofluorimeter.** H. Sprince and G. R. Rowley (Veterans Admin. Hosp., Coatesville, Pa., U.S.A.). *Science*, 1957, **125**, 25–26.—The activation and fluorescence maxima for soln. of quinine in 0·1 *N* H_2SO_4 are const. over the concn. range 0·005 to 10 μg per ml at 350 mμ (corrected) and 450 mμ, respectively. Within this range the calibration curve is linear from 0·005 to 0·1 μg per ml. A daily determination within the linear range is made to check the accuracy of the instrument. H. F. W. KIRKPATRICK

3195. **Photo-electric Fabry-Perot interferometer for assay of lead and uranium isotopes.** J. K. Brody, F. S. Tomkins and M. Fred (Argonne National Lab., Lemont, Ill., U.S.A.). *Spectrochim. Acta*, 1957, **8** (6), 329–347.—A Fabry-Perot interferometer combined with a spectrograph of moderate dispersion is used to conduct precise intensity measurements of the complex pattern of the Pb 4057·82-A line and then to determine the relative concn. of ^{208}Pb, ^{206}Pb, ^{204}Pb and ^{207}Pb in mixtures of all four isotopes. The results agree well with those from mass-spectrometric measurements. Low intensity of the hollow cathode source limited the usefulness of the interferometer method for U. E. G. CUMMINS

3196. **The use of the Rayleigh interferometer with volatile liquids.** J. J. Kipling (Chem. Dept., The University, Hull, England). *Hilger J.*, 1957, **3** (3), 35–37.—When the Rayleigh interferometer is used with volatile liquids a completely sealed cell is necessary. Bartell and Sloan (*J. Amer. Chem. Soc.*, 1929, **51**, 1637) used a mild-steel cover and mercury seal, but this is apt to rust and is liable to attack by some vapours. A cell has therefore been designed in which a glass block is stuck to the top of the cell to act as a cover. The cell is filled through two tapered holes in the block which can be closed with ground glass stoppers. K. A. PROCTOR

Thermal

3197. **Automatic thermobalance.** T. Damokos (Inorg. Chem. Dept., Tech. Univ., Budapest). *Magyar Kém. Foly.*, 1956, **62** (11–12), 383–386.—The thermobalance described records simultaneously the wt. *vs.* time and the temp. *vs.* time curves. The sample is supported in the centre of an electric furnace by means of a platinum wire attached to the beam of an analytical balance, which is placed underneath the furnace. A grey wedge, attached to the pointer of the balance, is interposed between the source of light and the photo-electric cell of the recording instrument. As the wedge moves, the amount of light falling on the cell varies. The non-linearity of the cell is compensated by making the wedge non-linear. Up to temp. between 200° and 250°, the design of the furnace ensures an approx. linear rate of heating without any control device, because the initial part of the exponential heating curve is nearly linear. The heating filament of the furnace is heated to a temp. two to three times higher than the desired final temp. of the furnace, and a thick insulating layer is interposed between the furnace and the heating element. For higher temp., a regulating device is used.
A. G. PETO

3198. **Improvements in the detection and estimation of the content of a given gas in a gaseous mixture by thermal conductivity.** Soc. Anon. des Manufactures des Glaces et Produits Chimiques de Saint-Gobain, Chauny et Cirey. Brit. Pat. 768,344; date appl. 10.3.52. France, date appl. 8.3.51.—The difference between the thermal conductivity of the gaseous mixture, *e.g.*, H in air, and that of another known gas of low thermal conductivity, *e.g.*, air, is used to produce a proportionate degree of unbalance in a Wheatstone bridge circuit, which includes a resistance element forming part of a detecting element exposed to the gaseous mixture and a corresponding resistance element forming part of a detecting element exposed to the known gas. The detecting elements comprise glass rods on which are wound wire resistors. The resistance elements are heated by d.c. or a.c. and the Wheatstone bridge circuit is supplied with a further electric current of audio-frequency, *e.g.*, from a resistance-capitance oscillator, separable from that of the heating current. The audio-frequency output is amplified and the amplifier is followed by a cathode-follower valve acting as an impedance-matching device. The amplified audio-frequency voltage is applied to a (recording) voltmeter and, if desired, a warning relay. In order to detect contents of H of the order of 1% with sufficient accuracy, a further amplification stage, consisting of a valve connected in the manner of a conventional resistance amplifier, is added. Without this additional amplification stage the voltages obtained in the measuring instruments for different percentages of H are 22, 18 and 10 V for proportions of H of 7, 4·98, and 3·85%, respectively. J. M. JACOBS

3199. **Determination of the content of gases in metals and alloys.** R. A. Karasev and A. Yu Polyakov. *Vestnik Akad. Nauk, SSSR*, 1954, (11), 61–62; *Ref. Zhur., Khim.*, 1956, Abstr. No. 75,354.—An apparatus has been evolved for the determination of gases in metals and alloys by vacuum fusion. Instead of glass tubing, tubes of stainless steel are used, of diam. 16 mm, joined with flanges. Only the quartz reaction tube and the observation window are joined with ground surfaces. Vacuum taps are replaced by mercury valves.
C. D. KOPKIN

See also Abstract 2993.

Electrical

3200. **Improvements in and relating to the measurement of concentration of oxygen in a liquid.** Cambridge Instrument Co. Ltd. (Inventor: G. Jessop). Brit. Pat. 767,959; date appl. 3.12.53.—The liquid is passed between two pairs of electrodes (housed in separate vessels), whilst small fixed potentials, but of different magnitudes, are maintained across the separate pairs of electrodes (mercury cathodes and silver-wire anodes). The higher potential is such that a change in oxygen concn. has a marked effect on the current flow, whilst the lower potential is such that the same change in oxygen concn. causes a much smaller change in the current flow. The difference between the currents flowing between the two pairs of electrodes is used to measure the oxygen concn. by means of a galvanometer calibrated directly in oxygen concn. With this differential system, it is found that most of the impurities commonly occurring in industrial water cause little interference. Lead salts alone cause an appreciable error; copper and iron salts affect both systems equally, and zinc salts have no effect. The apparatus is particularly suitable for the measurement of very small oxygen concn. (< 100 μg per litre) in boiler feed-water. J. M. JACOBS

3201. **Characteristics of stationary mercury electrode.** P. V. Peurifoy and W. G. Schrenk (Kansas Agric. Exp. Sta., Manhattan, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 410–414.—A stationary mercury electrode of small diameter, used in conjunction with a glass stirrer, is illustrated, and its usefulness, sensitivity, reproducibility and characteristics are investigated. The half-wave potentials determined were generally more negative than the corresponding potentials obtained with the dropping-mercury electrode and the diffusion currents two to four times greater. These values were determined for benzil, 1:3-dinitrobenzene, maleic acid, oxalic acid, Br^-, $S_2O_3^{2-}$, UO_2^{2+}, Cd^{2+}, Co^{2+}, Cu, Pb^{2+}, Sb, Sn^{2+} and Tl^+, and some results are given. E. G. CUMMINS

3202. **Analytical applications of the Barker square-wave polarograph. III. Orthophosphoric acid as a solvent and base electrolyte in direct inorganic polarographic analysis.** G. W. C. Milner and L. J.

Slee (A.E.R.E., Harwell, England). *Analyst*, 1957, **82**, 139–151.—Orthophosphoric acid in conjunction with other mineral acids that can be removed by heating (*e.g.*, HCl and HF) is a powerful solvent and then serves also as a base electrolyte for the direct polarographic determination of the constituents of the soln. Examples are given of the determination of Pb in tin, tin-base alloys, copper-base alloys, aluminium-base alloys, zinc alloys, monazite and other materials, and of Cu in lead-base, tin-base and aluminium-base alloys, of Zn in various types of non-ferrous alloys, and Cd in tin- and lead-base alloys. Usually no chemical separation after solution of the sample in H_3PO_4 is necessary. A. O. JONES

3203. **Electrochemical behaviour in anhydrous formic acid. I. The quinhydrone - formic acid electrode as a polarographic anode.** T. A. Pinfold and F. Sebba (Dept. of Chem., Univ., Cape Town, South Africa). *J. Amer. Chem. Soc.*, 1956, **78**, 2095–2096.—The quinhydrone electrode, when used in anhydrous formic acid, is found to be reversible, reproducible, and non-polarisable, irrespective of whether or not N is used to agitate the soln. The electrode is independent of quality or concn. of the quinhydrone and the salt effect is inappreciable. In addition it is not effected by small quantities of water. The formic acid analogue of the calomel electrode has been prepared. It is found that the potential of the quinhydrone - formic acid electrode *v.s.* the satd. calomel - formic acid electrode is $+ 0{\cdot}5384 \pm 0{\cdot}0005$ V at $25{\cdot}00° \pm 0{\cdot}01°$.
C. A. SLATER

3204. **Simple centrifugal filtration assembly for preparation of solid samples for radioassay.** F. Bronner and N. A. Jernberg (Rockefeller Inst. for Med. Res., New York, U.S.A.). *Anal. Chem.*, 1957, **29** (3), 462.—Results comparable to those of standard centrifugation - decantation techniques, but involving a single operation only, have been achieved with the centrifugal filtration device described. A planchette-sized filter is ready for counting on dismantling the apparatus, which fits standard centrifuges. E. G. CUMMINS

3205. **Estimating total absolute activity of small radioactive precipitates on filter-paper.** P. T. Wagner, L. R. Pollack and C. A. Donahoe, jun. (Industrial Lab., Mare Island Naval Shipyard, Vallejo, Calif., U.S.A.). *Anal. Chem.*, 1957, **29** (3), 405–408.—The estimate is made from the counts obtained from both sides of the paper. By means of a chart, based on exponential ppt. distribution, a relationship between the two counting rates and the total activity (counts per min. is obtained. Mathematical relationships are determined and explained. By using a filter-paper close to a windowless flow counter an accuracy within 10% of absolute values can be obtained.
E. G. CUMMINS

See also Abstract 2999.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.
ampere	amp.
Ångström unit	Å
anhydrous	anhyd.
approximate, -ly	approx.
aqueous	aq.
atmospher-e, -ic	atm.
boiling-point	b.p.
British thermal unit	B.Th.U.
calorie (large)	kg-cal.
calorie (small)	g-cal.
centimetre	cm
coefficient	coeff.
concentrated	conc.
concentration	concn.
constant	const.
corrected	(corr.)
crystalline, crystallised	cryst.
cubic	cu.
current density	c.d.
cycles per second	c/s
density	ρ
density, relative	d or wt. per ml
dilute	dil.
direct current	d.c.
distilled	dist.
ethylenediaminetetra-acetic acid	EDTA
electromotive force	e.m.f.
equivalent	equiv.
gram	g
gram-molecule	mole
half-wave potential	$E_{\frac{1}{2}}$
hour	hr.
hydrogen ion exponent	pH
infra-red	i.r.
insoluble	insol.
international unit	i.u.
kilogram	kg
kilovolt	kV
kilowatt	kW
liquid	liq.
maxim-um, -a	max.
melting-point	m.p.
microgram	μg (not γ)
microlitre	μl
micromole	μmole
micron	μ
milliampere	mA
milli-equivalent	milli-equiv.
milligram	mg
millilitre	ml
millimetre	mm
millimicrogram	mμg
millimolar	mM
millivolt	mV
minute (time)	min.
molar (concentration)	M
molecul-e, -ar	mol.
normal (concentration)	N
optical rotation	α_λ^t
ounce	oz
parts per million	p.p.m.
per cent.	%
per cent. (vol. in vol.)	%(v/v)
per cent. (wt. in vol.)	%(w/v)
per cent. (wt. in wt.)	%(w/w)
potential difference	p.d.
precipitate (as a noun)	ppt.
precipitated	pptd.
precipitating	pptg.
precipitation	pptn.
preparation	prep.
qualitative, -ly	qual.
quantitative, -ly	quant.
recrystallised	recryst.
refractive index	n_λ^t
relative band speed	R_y
relative humidity	r.h.
revolutions per minute	r.p.m.
saponification value	sap. val.
saturated calomel electrode	S.C.E.
second (time)	sec.
soluble	sol.
solution	soln.
specific gravity	sp. gr.
specific rotation	$[\alpha]_\lambda^t$
square centimetre	sq. cm
standard temp. and pressure	s.t.p.
temperature	temp.
ultra-violet	u.v.
vapour density	v.d.
vapour pressure	v.p.
volt	V
volume	vol.
watt	W
wavelength	λ
weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	$>$	less than	$<$
not greater than	$\ngtr$	not less than	$\nless$
is proportional to	$\propto$	of the order of, approximately	$\simeq$

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, *e.g.*, Fe^{II}, Mo^{V}. Substances in the ionic state are represented by Na^+, Fe^{3+}, Fe^{3+}, etc., for cations and by Cl^-, SO_4^{2-}, PO_4^{3-} etc., for anions.

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